University of Auckland

Physics 315: Classical and Statistical Physics

Statistical Physics

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Contents

Physics 315: Statistical Physics

You should be able to answer both qualitative and quantitative questions related to statistical thermodynamics applications.

You should already possess an intermediate physics background that includes the concepts and units of macroscopic thermodynamics, and classical statistical mechanics.

Lecture 1

1.1 Introduction

In Physics 231 we looked at classical thermodynamics mainly from a macroscopic viewpoint. Gases had temperature, pressure, and volume that were related by an equation of state. We worked with total quantities such as energy and entropy, and considered the work done by and on such systems, leading to heat engines and refrigerators. The main 'laws' of thermodynamics were expressed (postulated) in terms of these quantities. We also considered phase changes and basic radiation.

Along the way, we noted that explanations for thermodynamic behaviour required consideration at the atomic or molecular level. We used kinetic theory to explain pressure and some semblance of temperature, and discussed the Maxwell-Boltzmann distribution of velocities. In explaining the differences in heat capacity of real gases, and their change in temperature we introduced new concepts of internal energy that included the vibration and rotation of molecules. We noted the fundamental difference between energy exchange in the form of work, as compared to energy exchange by heating or cooling – involving ordered versus disordered molecules-consistent with statements of the Second Law. And we made the connection between the absorption and emission of radiation with the kinetic energy of molecules.

Much of the useful aspects of macroscopic thermodynamics can be applied without recourse to statistical physics. So why do we bother to study statistical physics, especially statistical thermodynamics?

We have already encountered some of the reasons: the heat capacities of real gases don't make much sense at a macroscopic level; the equation of state must be derived empirically; entropy still seems pretty vague as a macroscopic concept; blackbody radiation cannot really be explained macroscopically, etc.

One reason is to better explain classical thermodynamics. It should be possible to take our classical knowledge of individual atoms and molecules and derive the laws of macroscopic thermodynamics. We won't attempt this difficult task, but we will make heavy use of statistical thermodynamics to provide a much deeper insight as to why macroscopic thermodynamics works the way it does. By understanding classical thermodynamics from a molecular viewpoint, you will gain a better understanding of what is meant by thermodynamic equilibrium and entropy.

Another reason is to bridge the gap between Quantum Mechanics and Classical Thermodynamics. At their basic core, the energies of individual atoms or molecules are quantized, as is readily observed when we look at the emission spectra of atmospheric gases, for example. We should be able to take the quantum nature of matter into account when we build up the properties of very large numbers of atoms or molecules. We will find that this is in fact possible using the techniques of statistical physics, so that this provides an essential bridge between the quantum and macroscopic domains.

The above two reasons are perhaps sufficient in themselves, as they provide a deeper insight and understanding as to how things work. But it is also nice to show new results/insights that cannot be obtained otherwise. Statistical physics turns out to be essential for understanding phenomena as diverse as Brownian motion, spectroscopy, chemical kinetics, crystalline solids, etc.

In this course, we will first lay the foundations of equilibrium statistical thermodynamics by examining the probability of finding different microstates, the concept of a partition function, and the differences between identical and non-identical particles. We'll have a brief look at non-equilibrium conditions, and then look at some interesting applications.

From a single particle to the macroscopic collection

In even a small volume of gas, we have an astronomically large number of molecules: the Avogadro number of 6 x 10^{23} particles per mole comes to mind. While the physics of a single particle is very well understood, and in principle we could try to keep track of each particle in some futuristic supercomputer, this is not needed, and we can use the statistical power of massively large numbers to develop a theory that is remarkable precise at the macroscopic level. To do this we need to exploit some probabilistic concepts, and take advantage of the very large number of particles involved.

1.2   From Macroscopic (Classical) Thermodynamics

By considering a 'system' containing a large number of particles so that it has definable temperature, volume, density etc. we need only four 'laws' of thermodynamics.

Zeroth law: defines the concept of temperature and thermal equilibrium.

First law: formulates the principle of the conservation of energy for thermodynamic systems.

Second Law: (in its simplest form) heat flows spontaneously from high to low temperatures.

Third Law: the absolute zero of temperature is not attainable.

We can also define thermal equilibrium:
- In a thermally isolated system, thermal equilibrium is achieved when the system properties become independent of time.
- Two systems in thermal contact are in thermal equilibrium when there is no net flow of energy between them.

Two systems in thermal equilibrium have the same temperature. They can also be in thermodynamic equilibrium. For this to occur they must also be in

- Mechanical equilibrium with no unbalanced forces acting ($p_1 = p_2$)

- Chemical equilibrium with no reactions occurring ($\mu_1 = \mu_2$)

The bulk state of a macrosystem in equilibrium is defined by its equation of state. This relates its bulk properties and its temperature. e.g. for an ideal gas $pV = NkT$.

From the 1st law we had the concept of energy conservation and the existence of internal energy, $U_2 - U_1 = Q_{tot} + W_{tot}$.

From the 2nd law we had the concept of entropy, irreversibility and the unattainability of some energy states,

$$TdS = dU + pdV \qquad \Delta S_{\text{universe}} \geq 0 \qquad S = k \ln W$$

We define enthalpy, $H = U + pV$

We define specific heats, $C_V = \frac{\partial U}{\partial T}$, $C_P = \frac{\partial H}{\partial T}$

The Gibbs free energy, $G = U - TS + pV = H - TS$

The Helmholtz free energy, $A = U - TS$

1.3 Macroscopic Postulates

Laurendeau, Appendix F

At the macroscopic level, we postulate that a simple system is completely characterized by its internal energy, U, its volume, V, and the number of particles, N_1, N_2, ... of the different chemical components. We also postulate the existence of a function of these parameters (U, V, N_i), called entropy that is a continuous, differentiable, monotonically increasing function of the internal energy, U.

$$S = S(U, V, N_i)$$
$$U = U(S, V, N_i)$$

Taking the total derivative of U, we have

$$dU = \frac{\partial U}{\partial S}dS + \frac{\partial U}{\partial V}dV + \sum_{i=1}^{k} \frac{\partial U}{\partial N_i}dN_i$$

We can now define temperature, pressure and the chemical potential as

$$T = \frac{\partial U}{\partial S} \qquad p = -\frac{\partial U}{\partial V} \qquad \mu_i = \frac{\partial U}{\partial N_i}$$

So that

$$dU = TdS - pdV + \sum \mu_i dN_i \tag{1.1}$$

and

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \sum \frac{\mu_i}{T}dN_i \tag{1.2}$$

The familiar concepts of macroscopic thermodynamics can be retrieved from these postulates. For example, consider an isolated system with two subsystems in thermal contact, with internal energies and entropies, $U_{1,2}$ and $S_{1,2}$, free to change such that

$$U_1 + U_2 = \text{constant} \tag{1.3}$$

In equilibrium, we postulate that the entropy is a maximum, so that

$$dS = dS_1 + dS_2 = 0$$

From (1.2)

$$dS = \frac{1}{T_1}dU_1 + \frac{1}{T_2}dU_2 = 0 \tag{1.4}$$

so that from (1.3), noting

$$dU_1 = -dU_2 \qquad \frac{1}{T_1} = \frac{1}{T_2} \qquad T_1 = T_2 \tag{1.5}$$

So that thermal equilibrium implies equality of temperature, as expected. Continuing with the other macroscopic thermodynamic potentials, we have

$$dH = dU + pdV + Vdp \tag{1.6}$$

From (1.1)

$$dH = TdS + Vdp + \sum_i \mu_i dN_i \tag{1.7}$$

So that

$$T = \frac{\partial H}{\partial S} \qquad V = -\frac{\partial H}{\partial p} \qquad \mu_i = \frac{\partial H}{\partial N_i}$$

Similarly, from G and A,

$$V = \frac{\partial G}{\partial p} \qquad S = -\frac{\partial G}{\partial T} \qquad \mu_i = \frac{\partial G}{\partial N_i}$$

$$p = -\frac{\partial A}{\partial V} \qquad S = -\frac{\partial A}{\partial T} \qquad \mu_i = \frac{\partial A}{\partial N_i}$$

Lecture 2: Probabilities

2.1 Review of Basics

The most common form of probability is as the relative frequency of occurrence. In other words, in a series of N discrete events, if outcome A happens x times, the probability of A can be written $P(A) = \frac{x}{N}$.

If we don't have the luxury of experience, we can still assign a probability to A occurring based on best knowledge, but that type of probability (subjective or Bayesian) will not be used here.

Example.
The probability of drawing a Jack randomly from a standard deck of 52 cards is $P(\text{Jack}) = 4/52$.

The probability of picking a Jack or a Queen would be $= 4/52 + 4/52 = P(\text{Jack}) + P(\text{Queen})$

The probability of picking a Jack and a Queen in succession from the same deck would be $= 4/52 \times 4/51$, or from different decks $= 4/52 \times 4/52$.

The probability of being dealt a Jack and a Queen in a two card deal is $(4/52 + 4/52) \times 4/51$.

Permutations and Combinations

Take 4 aces out of a deck of cards, and randomly pick each ace in sequence. How many different ways could this occur? ($4 \times 3 \times 2 \times 1 = 24$ permutations$=4!$).

What if you just wanted any 4 aces? (1 combination$=4!/4!$).

More generally, picking M cards from a deck of N, without replacement has $N \times (N - 1) \times ... \times (N - M + 1)$ permutations $P(N, M) = \frac{N!}{(N-M)!}$. Note that $0! = 1$.

On the other hand, if replacements are allowed, the number of permutations is N^M. Note that if N is very large compared to M, the difference between replacement and non-replacement is small.

Similarly the number of combinations of M cards taken from a deck of N without replacement is given by $C(N, M) = \frac{P(N,M)}{M!} = \frac{N!}{M!(N-M)!}$, since there are $M!$ ways to rearrange the cards within each combination, and this rearrangement does not affect the combination.

What about dividing N into two distinct groups, with M having characteristic A, and $(N - M)$ having characteristic not-A. There are $N!$ ways of arranging the entire set, $M!$ redundant ways of arranging the A group, and $(N - M)!$ ways of arranging the not-A group. The total number of different unique arrangements into A and not-A is then $= \frac{N!}{M!(N-M)!} = C(N, M)$.

1. How many different ways can a deck of 52 cards be shuffled? 8.066×10^{67}

2. A hand of whist contains 13 cards. How many different hands are possible? 6.35×10^{11}.

3. In a game of whist, all the cards are dealt out into 4 hands, each with 13 cards. How many different games of whist can be dealt, noting that the ordering of hands between players matters? 5.36×10^{28}

2.2 Stirling's Approximation

We seek

$$\ln N! \approx N \ln N - N \tag{2.1}$$

$$\ln N! = \sum_{n=1}^{N} \ln n \tag{2.2}$$

We can approximate this by the integral

$$\ln N! \approx \int_{0}^{N} \ln n \, dn = [n \ln n - n]_{0}^{N} \tag{2.3}$$

To find the lower limit at $n = 0$, use l'Hopital's rule

$$\lim_{n \to 0}(n \ln n) = \left[\frac{d(\ln n)}{d(1/n)}\right]_{n=0} = \left[\frac{1/n}{-1/n^2}\right]_{n=0} = 0 \tag{2.4}$$

Giving Stirling's Approximation.

2.3 Discrete vs Probability Density Function

Discrete Probabilities

Consider discrete outcomes x_i, $i = 1, 2, ..., N$ such that

$$\sum_{i=1}^{N} P(x_i) = 1$$

we can define the mean of this distribution as

$$\bar{x} = \langle x_i \rangle = \sum_{1}^{N} P(x_i) x_i$$

This is also what we mean by the expected value, $E(x) = \bar{x}$, also written as $\langle x \rangle$ and the variance is

$$\sigma^2 = \sum_{i}(x_i - \bar{x})^2 P(x_i)$$

Continuous Probabilities

Using a probability density function $f(x)$, we have

$$\int_{-\infty}^{\infty} f(x)dx \equiv 1$$

if there is no limit on the values of x. Note that $f(x)$ by itself does not represent a probability. Rather it is referred to as a pdf or a probability density function.

Instead $\int_a^b f(x)dx$ represents the probability of x being in the range a to b.

Cumulative Probability

$$F(x) = \int_{-\infty}^{\infty} f(x')dx'$$

Whence $P(a \leq x \leq b) = F(b) - F(a)$

2.4 Binomial Distributions

Here we consider only two possible outcomes of a trial, A or B, with probabilities of occurrence, p and q, respectively. That is, $p + q = 1$. If we draw N independent samples, the probability of getting M cases of A, and $(N - M)$ cases of B is then $p^M q^{N-M}$ in a particular sequence. If we are not concerned about the order in which A and B occur, then we must consider the number of unique arrangements of M from N, or $C(N, M)$. Thus the total probability of drawing M cases of A using N trials, regardless of the order of the sequence (we don't mind when the M appear in the sequence) is given by

$$B(M) = C(N, M)p^M q^{N-M} = \frac{N!}{M!(N-M)!}p^M q^{N-M} \tag{2.5}$$

which is the binomial probability distribution.

You may want to show the following results:

- Expected number of M from N trials $= Np$

- Expected variance in the distribution of M about its mean $= Npq$

The relative width of the distribution, given by the ratio of the standard deviation to the expected value is thus

$$\frac{\sqrt{Npq}}{Np} = \sqrt{\frac{q}{Np}}$$

which clearly gets narrower as N increases.

2.5 Poisson Distributions

Consider the extension of $B(M)$ as $N \to \infty$ and $p \to 0$. Writing $\mu = \bar{M} = Np$, and $q = 1 - p$, we have from (2.5)

$$B(M) = \frac{N(N-1)...(N-M+1)}{M!}\left(\frac{\mu}{N}\right)^M (1-p)^{N-M}$$

$$\lim_{N \to \infty} B(M) = \frac{N^M}{M!}\left(\frac{\mu}{N}\right)^M (1-p)^N = \frac{\mu^M}{M!}(1-p)^{\frac{\mu}{p}}$$

Using the useful relation

$$\lim_{p \to 0}(1-p)^{\frac{1}{p}} = e^{-1}$$

we have as $N \to \infty$ and $p \to 0$,

$$P(M) = \frac{e^{-\mu}\mu^M}{M!} \tag{2.6}$$

which is the Poisson distribution.

This has standard deviation

$$\sigma = \sqrt{Np} = \sqrt{\mu}$$

The Poisson distribution is a good approximation to the binomial distribution for $\mu = Np \ll \sqrt{N}$.

2.6 Gaussian Distribution

As $N \to \infty$ for finite p, the Binomial distribution tends to the Gaussian distribution. After some mathematical manipulation (which we will take as given) we find

$$\lim_{N \to \infty} B(y) = G(y) = \frac{1}{\sqrt{2\pi Npq}}\exp\left(-\frac{y^2}{2Npq}\right) \tag{2.7}$$

where $y = M - \bar{M} = M - Np$.

Remembering that $\sigma^2 = Npq$, and defining $\frac{y}{\sigma}$, we have the canonical form

$$G(z) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{z^2}{2}\right) \tag{2.8}$$

The Gaussian distribution is a good approximation to the binomial distribution, provided $Np > 5$ and $Nq > 5$.

We can use it to find the probability that z lies in some range, $z_1 < z < z_2$, namely

$$P(z_1 < z < z_2) = \frac{1}{\sqrt{2\pi}}\int_{z_1}^{z_2}\exp\left(-\frac{z^2}{2}\right)dz \tag{2.9}$$

The Gaussian is characterised by its symmetry about the mean. It is referred to as the bell curve, and has so many applications its values are tabulated in many texts.

2.7 Combinations Relevant to Statistical Thermodynamics

We will be concerned with the different energy levels that a molecular system can occupy. We may find that there can be a finite number of energy states in a given energy level. (Imagine the energy levels as a set of shelves, with higher shelves indicating greater energy. Because the energy levels are quantized, each shelf occupies a unique height. On each shelf there can be a finite number of baskets. The baskets represent the number of energy states possible at that energy level. Within each basket we may find at most one fermion, or an unlimited number of bosons.)

Occupying these energy states is akin to arranging objects in groups. Hence our interest in permutations and combinations. We may have N objects (molecules) placed in M baskets (energy states). From a classical perspective, the objects will usually be distinguishable. From a quantum perspective, the fundamental particles may well be indistinguishable. Also, from a quantum perspective, the population of a given energy state may be limited (fermions) or unlimited (bosons).

The number of possible energy states g_i of the ith energy level is termed its degeneracy.

2.7.1 Distinguishable Objects

All classical objects tend to be distinguishable. Consider the following examples.

1. N distinguishable objects place in M containers with a limit of one object per container. We must have $M > N$. Object 1 can be placed M different ways, 2 can be placed $(M - 1)$ ways, etc.

$$\begin{aligned} W_1 &= M(M-1)(M-2)...(M-N+1) \\ &= \frac{M!}{(M-N)!} \end{aligned} \tag{2.10}$$

2. N distinguishable objects placed in M containers such that the ith container holds N objects. We can arrange the N objects $N!$ ways. Within each of the M containers, however, the arrangement is irrelevant (we just need the number N_i), so we must discount $N_i!$ permutations within each container. The total number of ways for this example is therefore

$$W_2 = \frac{N!}{\prod\limits_{i=1}^{M} N_i!} \tag{2.11}$$

where $\prod\limits_{i=1}^{M} N_i! = (N_1!)(N_2!)...(N_M!)$

3. N distinguishable objects arranged in M containers with no limitation on the number in each container.

$$W_3 = M^N \tag{2.12}$$

2.7.2 Indistinguishable Objects

4. Similar to 1, arrange N objects in M containers, with a limit of one per container. This is similar to eq. (2.10), but because the objects are indistinguishable there must be fewer cases as any rearrangement among the N objects would not be detectable. They can be rearranged among themselves $N!$ ways, giving

$$W_4 = \frac{M!}{N!(M-N)!} \tag{2.13}$$

5. Now place the N objects into the M containers without restricting the number in each container. This requires a fresh approach (we can't simply adapt eq. (2.12)). Consider the objects initially distinguished by numbers from 1 to N, with the M containers acting as partitions between the numbers. e.g. 1, 2, 3, |, 4, 5, |, 6, |...|$N-1$, N (1,2,3) in container 1, to $(N-1, N)$ in container M. There are $N+M-1$ objects plus partitions that can be arranged $(N+M-1)!$ ways. However, since the objects are really indistinguishable there are $N!$ permutations that are undetectable, and similarly interchanging the partitions can't be detected, giving another factor of $(M-1)!$, so that

$$W_5 = \frac{(N+M-1)!}{N!(M-1)!} \tag{2.14}$$

Eqs (2.12), (2.13) and (2.14) will correspond to Boltzmann, Fermi-Dirac and Bose-Einstein statistics, respectively.

Lecture 3: Examples: Microstates and Macrostates

3.1 Examples Following Section 2.7

Let us consider the number of ways of placing 2 coins into 3 fountains, following Boltzmann, Fermi-Dirac, and Bose-Einstein statistics. That is, $N = 2$, $M = 3$.

a. For Boltzmann we consider the coins to be distinguishable. $W_B = M^N = 3^2 = 9$ (show this with a figure)

b. For Fermi-Dirac, the coins are identical, with at most one per fountain. $W_{FD} = \frac{M!}{N!(M-N!)} = \frac{3!}{2!(3-2)!} = 3$ (show this with a figure)

c. For Bose-Einstein, the placement is unrestricted, but the coins are identical. $W_{BE} = \frac{(N+M-1)!}{N!(M-1)!} = \frac{4!}{2!2!} = 6$ (show this with a figure)

3.2 Essential Concepts from Quantum Mechanics

The energy of an atom or molecule is quantized, ε_j. The energy levels are not necessarily equally probable. Any given energy level may have an associated degeneracy, g_i, representing the number of energy states associated with that energy level. Each energy state may have a unique set of quantum numbers, and be equally likely at some fixed energy level. In addition, we need to know whether the particle can be considered distinguishable or indistinguishable. Gas particles are generally indistinguishable. Atoms forming a

crystalline solid, by contrast, are usually distinguishable. We also need to know whether the particle can share the same set of quantum numbers (bosons) or whether each must have a unique set of quantum numbers (fermions).

3.3 Ensembles We May Need

Initially we work with independent particles (e.g. an ideal gas). Even with this restriction, we develop an improved understanding of the basic thermodynamic concepts of entropy, thermodynamic equilibrium, and the significance of temperature to the definition of thermal equilibrium.

Before continuing with independent particles, we pause briefly to note the more general concepts of ensembles, that may include dependent particles. These were developed by Gibbs to provide a strong theoretical basis for statistical thermodynamics that would be reasonably general.

An ensemble is a theoretical collection of a very large number η of systems, each of which replicates the macroscopic thermodynamic system under investigation.

There are three main types of ensembles.

The microcanonical ensemble is composed of η isolated systems (N, V, U) for which the total number, N, the volume, V, and the internal energy, U , are the replicated thermodynainic properties.

The canonical ensemble is composed of η closed, isothermal systems (N, V, T), for which the total number, N, the volume, V, and the temperature, T, are the independent thermodynamic parameters.

The grand canonical ensemble is composed of η open, isothermal systems (μ, V, T), for which the chemical potential μ, the volume V, and the temperature T, are the constant independent variables.

We can now introduce the two basic postulates of statistical thermodynamics (according to Gibbs).

1. The time average of a system thermodynamic variable is equal to the ensemble average, which is the average over the instantaneous values of the variable in each member of the ensemble as $\eta \to \infty$.

2. For an isolated thermodynamic system, the members of the ensemble are distributed with equal probability over the possible system quantum states defined by specification of N, V and U.

The first postulate is the ergodic hypothesis that equates temporal and ensemble averages, and may be encountered in other branches of physics.

The second postulate is the principle of equal a priori probability, whereby each member of the ensemble is equally likely to occur in an isolated system.

3.4 Maxwell-Boltzmann Method (M-B)

We start with an isolated system of independent particles. We can relate this to the Gibbs ensemble by making each member of the ensemble a single particle (i.e. $N = \eta$) . The system constraints are

$$N = \sum_j N_j = \text{constant}$$

$$U = E = \sum_j N_j \varepsilon_j = \text{constant}$$

The specification of the N_j is called the particle distribution, that is the number of particles in each energy level. Any particular such distribution is called a macrostate. Within each macrostate we could also refer to the distribution of particles within each energy state, taking account of the influence of degeneracy. Each such distribution is termed a microstate. For any macrostate there may be many possible microstates. The most probable distribution of particles will correspond to the macrostate with the greatest number of microstates.

We can now rephrase the Gibbs postulates in terms of the M-B method.

1. The time average for a thermodynamic variable is equivalent to its average over all possible macrostates.

2. All microstates are equally probable; hence, the relative probability of each macrostate is given by the number of its microstates.

3.5 M-B Examples With Different Energy Levels

1. Consider $N = 3$ distinguishable particles, sharing 3 quanta of energy. We can consider a ground shelf of zero energy, and three equally spaced shelves above. There are three main configurations: (a) one particle could be on the top shelf, with the other two on the bottom; (b) all three on shelf 1; (c) one on shelf 1 and one on shelf 2. Of these, (a) can happen 3!/2! ways, (b) 3!/3! ways , and (c) 3!/1! ways. For each of these, the 3 particles can be arranged with 3! permutations, but whenever more than 1 particle is on the same shelf, the arrangement on that shelf does not matter, hence the different denominators (cf. eq. 2.11). (show this with a figure).
So for this example, there are 10 microstates, with configuration (c) being the most likely, with 60% of the total.

Lecture 4: Boltzmann Distribution

4.1 Maxwell-Boltzmann Examples with Different Energy Levels

2. Moving to the more general case of N distinguishable particles distributed across M energy levels such that η_i occupy the ith level, we are back at Eq. (2.11)

$$W = \frac{N!}{\prod_{i=1}^{M} \eta_i!} \tag{4.1}$$

Each configuration gives a unique arrangement of η_i, so W will in general vary from configuration to configuration. For small N we can evaluate eq. (4.1) directly. For large N, Stirling's approximation in its simplest form is helpful

$$\ln N! \approx N \ln N - N \tag{4.2}$$

3. Same thing, but with $N = 5$, sharing 5 quanta. Using eq. (4.1), configuration (a) has 5 on shelf 1 ($W = 5!/5! = 1$), (b) 4 on shelf 0, 1 on shelf 5 ($W = 5!/4! = 5$); (c) 3 on shelf 0, 1 on shelf 1, 1 on shelf 4 ($W = 5!/3! = 20$); (d) 3 on shelf 0, 1 on shelf 2, 1 on shelf 3 ($W = 5!/3! = 20$); (e) 2 on shelf 0, 2 on 1, 1 on 3 ($W = 5!/2!2! = 30$); (f) 2 on 0, 1 on 1, 2 on 2 ($W = 5!/2!2! = 30$); (g) 1 on 0, 3 on 1, 1 on 2 ($W = 5!/3! = 20$). That is, a total of 126 microstates.

4. Now consider adding another 5 particles to the previous examples, but keeping the total energy constant. That is add 5 to shelf 0. $N!$ is now 3,628,800, and the peak configuration (g) has $10!/6!3! = 840$ microstates. Altogether there are now 2002 microstates, so configuration (g) has 42% of these.

4.2 Examples With 2 Non-degenerate Energy Levels

Take $N = 6$ particles and place into $M = 2$ non-degenerate energy levels with no limit to the number in any level.

1. For indistinguishable particles.
According to eq. (2.10), $W_m = \frac{(N+M-1)!}{N!(M-1)!} = N + 1 = 7$. Check by noting the possible configurations range from 0 in level 1 and 6 in level 2, to 6 in level 1 and 0 in level 2.

2. For distinguishable particles.
According to eq. (2.7),
$$W_d = \frac{N!}{\prod_{i=1}^{M} N_i!} = \frac{6!}{N_1! N_2!}$$
This gives $W_d = 1, 6, 15, 20, 15, 6, 1$ for the 7 different configurations, for a total of 64.
This total can also be obtained from eq. (2.12), $W_d = M^N = 2^6 = 64$.
Total $W = 64$; most probable $W = 20$; mean $W \approx 9$.

3. Now consider very large $N = 10^{23}$, keeping $M = 2$.

$$W_{tot} = 2^N \qquad \bar{W} = \frac{2^N}{N+1}$$

That is, $\ln W = N \ln 2 \approx 7 \times 10^{22}$; $\ln \bar{W} = N \ln 2 - \ln(N+1) \approx 7 \times 10^{22} - 53$.
So, very little difference between the total number of microstates and the mean number (and also the most probable number).
We have

$$\lim_{N \to \infty} \frac{\ln W_{mp}}{\ln W_{tot}} = 1$$

For large N, the only significant microstate is the most probable one. From the point of view of classical thermodynamics, the most probable particle distribution must represent the equilibrium particle distribution.

4.3   The Effect of Increasing N

Because of the factorial, the number of permutations grows very rapidly with the number of particles. The number of microstates in most configurations increases accordingly, as does the total number of microstates. Fortunately, we don't need to do the arithmetic, as the answer becomes meaninglessly large for, say, Avagadro's number of particles. Even terms like googol (10^{100}) or googolplex ($10^{10^{100}}$) cannot keep up. What we are left with is that for macroscopic numbers of particles, not only is there a ridiculously large number of microstates, but the most probable configuration of these also becomes so overwhelmingly the favourite that the others can be totally ignored.

Again, by noting that the relative width of the Gaussian distribution is proportional to $1/\sqrt{N}$, for large N, this becomes vanishingly narrow.

Our next task then, is to develop a way of identifying the most popular configuration of microstates, knowing there is some point in finding it.

We saw last time that for a large enough system, there was really only one significant microstate. Now we will find the Boltzmann distribution that this corresponds to.

4.4   Uniformly Spaced Energy Levels

We have, as before, N identical distinguishable particles, distributed amongst many containers that will now correspond to different energy levels. We will take these energy levels to be quantized, and label successive levels as $...j, k, l, m, n, o, ...$ corresponding to energies $...\varepsilon_j, \varepsilon_k, \varepsilon_l, \varepsilon_m, \varepsilon_n, \varepsilon_o, ...$ initially assumed to be equally spaced.

For a given distribution, with

$$N = \sum_i n_i$$

and

$$E = \sum_i n_i \varepsilon_i$$

fixed, the number of microstates for any given configuration will be

$$W = \frac{N!}{\prod_i n_i!} = \frac{N!}{...n_k! n_l! n_m! n_n! n_o!...} \tag{4.3}$$

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We can make a minimal perturbation to this configuration by shifting one particle down from level n to level m, and one up from level l to level m, so that E is unchanged. This gives a perturbed weight of

$$W' = \frac{N!}{...n_k!(n_l - 1)!(n_m + 2)!(n_n - 1)!n_o!...} \tag{4.4}$$

Let us take the original W to be the most probable configuration. This means that for a small perturbation $\delta\chi$ in configuration about this most probable value, $\frac{\delta W}{\delta\chi} = 0$. This allows us to set $W' \approx W$.

Equating (4.3) and (4.4) gives

$$(n_l - 1)!(n_m + 2)!(n_n - 1)! = n_l!n_m!n_n!$$

So that

$$n_l n_n = (n_m + 2)(n_m + 1)$$

And because all the numbers are very large, we have

$$\frac{n_l}{n_m} = \frac{n_m}{n_n}$$

Extending this to all consecutive levels, we get a geometric progression in the population numbers, so that

$$... = \frac{n_j}{n_k} = \frac{n_k}{n_l} = \frac{n_l}{n_m} = \frac{n_m}{n_n} = \frac{n_n}{n_o} = ... \tag{4.5}$$

So, once we have the population ratio between any two consecutive energy levels, we will have the answer for all levels.

4.5 Non-Uniformly Spaced Energy Levels

Consider *any* three levels, l, m, and n, with energies $\varepsilon_l, \varepsilon_m$ and ε_n. These can be arbitrary levels, not even necessarily adjacent. We designate the two energy spacings as being in some ratio

$$\frac{\varepsilon_n - \varepsilon_m}{\varepsilon_m - \varepsilon_l} = \frac{p}{q} \tag{4.6}$$

where p and q are small integers (relative to n_i). Rearranging, we have

$$(p + q)\varepsilon_m = p\varepsilon_l + q\varepsilon_n$$

Our perturbation, keeping N and E constant as before, is to subtract $(p + q)$ particles from level m, to add p to level l, and to add q to level n.

Analogous to eq. (4.4), we now have

$$W' = \frac{N!}{...(n_l + p)!(n_m - p - q)!(n_n + q)!...} \tag{4.7}$$

Equating (4.3) and (4.7) gives

$$\frac{(n_l + p)!}{n_l!} \frac{(n_n + q)!}{n_n!} = \frac{n_m!}{(n_m - p - q)!}$$

Or

$$[(n_l + p)(n_l + p - 1)...(n_l + 1)][(n_n + q)(n_n + q - 1)...(n_n + 1)] \tag{4.8}$$
$$= (n_m + p + q)(n_m + p + q - 1)...(n_m + 1)$$

Again assuming large numbers, so that $n_l \gg p$, and $n_m \gg p + q$, eq. (4.8) becomes

$$n_l^p n_n^q = n_m^{p+q}$$

or

$$\left[\frac{n_l}{n_m}\right]^p = \left[\frac{n_m}{n_n}\right]^q \tag{4.9}$$

Eq. (4.9) reduces to eq. (4.5) if $p = q$, but is far more general, as it applies to any three arbitrary energy levels.

Taking the natural logarithm of eq. (4.9) gives

$$p \ln \frac{n_l}{n_m} = q \ln \frac{n_m}{n_n} \tag{4.10}$$

From eq. (4.6) we have

$$\frac{1}{\varepsilon_m - \varepsilon_l} \ln \frac{n_l}{n_m} = \frac{1}{\varepsilon_n - \varepsilon_m} \ln \frac{n_m}{n_n} = \text{constant} \tag{4.11}$$

Since the choice of levels is quite arbitrary, eq. (4.11) fixes the relative population of any two energy levels, taking into account the difference in energy of the two levels, to some constant value. Writing this constant as β, we have

$$\frac{1}{\varepsilon_m - \varepsilon_l} \ln \frac{n_l}{n_m} = \beta$$

and

$$n_l = n_m \exp(\beta(\varepsilon_m - \varepsilon_l)) \tag{4.12}$$

We can make one of the levels the ground state, with $\varepsilon_0 = 0$, containing n_0 particles. The population of any energy level ε_i then gives the Boltzmann distribution

$$n_i = n_0 e^{-\beta \varepsilon_i} \tag{4.13}$$

4.6 The Unlikelihood of Other Configurations

We have already suggested that the most probable configuration accounts for almost all the possible microstates. This can now be shown quantitatively, by examining a slight perturbation to the Boltzmann distribution.

Setting

$$\alpha_i = \frac{n_i' - n_i}{n_i} \tag{4.14}$$

as the relative difference in the population of the ith level, where n_i' is the perturbed value,

$$\sum_i \alpha_i n_i = 0$$

with the constraints

$$\sum_i \alpha_i n_i \varepsilon_i = 0$$

after some analysis (see Nash p. 20-21 for the details if you are interested), we find

$$\ln \left(\frac{W_{max}}{W} \right) = \sum_i n_i \alpha_i^2 = N \alpha_{rms}^2 \tag{4.15}$$

That is,

$$W = W_{max} e^{-N\alpha_{rms}^2} \tag{4.16}$$

In other words, the weight of a perturbed macrostate, compared with the most probable one, drops off exponentially with the number of particles and the rms fractional perturbation. Noting that for molar quantities, where $N \approx 10^{23}$, even an rms perturbation of 1 in 10^9 yields a macrostate that is negligibly weighted compared with $W_{max} \approx \exp(-10^5)$. Alternatively, the most probable configuration forms a predominant-group (PG) configuration, the members of which are perturbed so slightly from one another that the difference is immeasurable.

Lecture 5: Corrected Boltzmann, B-E and F-D

5.1 Equilibrium

Consider an isolated macroscopic system comprised of identical but distinguishable units that are weakly coupled (i.e. able to exchange energy with each other while maintaining the quantum states they would have an isolation.) We can generalize the concept of the PG configuration to this more complex system by applying the postulates of statistical thermodynamics.

The system is equally likely to be in any one of its microstates in any given instant.

The overwhelming probability is that it will be found in its PG configuration.

The overwhelming probability is that it will always be found in the one macroscopic state that corresponds to its PG configuration.

The number of microstates in this configuration, W_{max} is often called the thermodynamic probability.

Even though it is capable of change (other microstates) the unchanging nature of the PG configuration of the system means it is in an equilibrium state.

At equilibrium, the configuration of an isolated macroscopic assembly is typically that described by the Boltzmann distribution law.

If initially in a macrostate that has $W < W_{max}$, the assembly would not be in equilibrium, and we would expect it to change configuration until W_{max} is reached. This configuration may also be viewed as the one that has maximum disorder.

5.2 W and Energy, E

W will change as the total energy, E, of the system changes.

Consider the baseline state of our isolated macroscopic assembly of identical but distinguishable, weakly coupled units. These could be the atoms in a crystal lattice, that oscillate like harmonic oscillators. We have as before

$$W = \frac{N!}{\prod_i n_i!} \tag{5.1}$$

and

$$n_i = n_0 \exp(-\beta \varepsilon_i) \tag{5.2}$$

Taking the log of eq. (5.1),

$$\ln W = \ln N! - \sum_i \ln n_i! \tag{5.3}$$

and

$$d \ln W = -\sum_i d \ln n_i! \tag{5.4}$$

The derivative of Stirling's forumla gives

$$d \ln N! = d(N \ln N) - dN$$
$$= \ln N dN \tag{5.5}$$

So that

$$d \ln W = -\sum_i \ln n_i dn_i \tag{5.6}$$

From eq. (5.2)

$$\ln n_i = \ln n_0 - \beta \varepsilon_i \tag{5.7}$$

Thus eq. (5.6) becomes

$$d \ln W = -\ln n_0 \sum_i dn_i + \beta \sum_i \varepsilon_i dn_i \tag{5.8}$$

That is,

$$d \ln W = \beta dE \tag{5.9}$$

because the total number of units is constant, and the weak coupling means that each ε_i is constant so that the energy depends only on the populations of each level.

We can't assume that β will remain constant as the energy changes, as has been done implicitly in eq. (5.8). So eq. (5.9) is only for infinitesimal changes.

5.3 Approaching Thermal Equilibrium

Consider two macroscopic systems, X and Y, that are brought into thermal contact. The microstates of the combined system will be the product $W_X \cdot W_Y$ of the microstates of X and Y. This will initially be $W_{Xi} \cdot W_{Yi}$, but this product will increase to a new maximum as the two systems come into equilibrium. In general

$$d(W_x \cdot W_Y) \geq 0 \tag{5.10}$$

with the equality implying equilibrium. That is,

$$d \ln W_X + d \ln W_Y \geq 0 \tag{5.11}$$

From eq. (5.9) we have

$$\beta_X dE_X + \beta_Y dE_Y \geq 0 \tag{5.12}$$

From the conservation of energy, we have $dE_X + dE_Y = 0$, so that

$$(\beta_X - \beta_Y) \, dE_X \geq 0 \tag{5.13}$$

If X is hotter than Y, energy will leave X and enter Y. dE_X will be negative, and therefore $\beta_Y \geq \beta_X$. Also $dW_X \leq 0$ implying a reduction in the number of microstates for X, with a corresponding increase for Y.

Clearly $\beta_X = \beta_Y$ implies no energy exchange, meaning that X and Y are in thermal equilibrium.

β must therefore be some inverse function of temperature.

From dimensional consideration of eq. (5.9), β has units of energy^{-1}, so that its simplest form would be

$$\beta = \frac{1}{kT} \tag{5.14}$$

where k is some constant with units of J K^{-1}.

5.4 Absolute Zero

In the limits as $T \to 0$. $\beta \to \infty$, and eq. (5.2) tells us that for all non-zero energy levels the populations of those levels all tend to 0. The ground state is defined to be $\varepsilon_0 = 0$ and the entire population tends to this state.

5.5   Entropy and Microstates

Again considering X and Y reaching equilibrium, we noted that the combined microstates are given by $W_{XY} = W_X \cdot W_Y$, so that $\ln W_{XY} = \ln W_X + \ln W_Y$. If we define a property of the system to be $\$ = \ln W$, then $\$_{XY} = \$_X + \$_Y$ is an extensive property of the system, like volume and energy, unlike pressure and temperature. Anticipating the connection with the macroscopic definition of entropy, we instead define

$$S = k \ln W \tag{5.15}$$

to be the property of the system that is a measure of the number of microstates, and call this the entropy. k is the same constant as in eq.(5.14), but we have yet to demonstrate that connection.

S is also an extensive property of the system. It also reaches a maximum when the (isolated) system has reached equilibrium. To show why it is a better choice than $\$$, consider from eq. (5.9),

$$k d \ln W = k \beta dE$$

Then, from eq. (5.14),

$$dS = \frac{dE}{T}$$

which is the familiar macroscopic definition. Here we must keep volume constant and require that changes in E are due only to heat transfer.

Again consider the minimum value of T, where everything tends to the ground state. For this,

$$S_0 = k \ln W_0 = k \ln \left(\frac{N!}{\prod_i n_i!} \right) = k \ln \left(\frac{N!}{N!} \right) = 0$$

5.6   The Inclusion of Degeneracy

Eq. (5.2) is based on unique energy levels that have no degeneracy. i.e. $g_i \equiv 1$. This applies in some cases, but more generally the energy levels will be degenerate. While this is mainly of relevance to the Fermi-Dirac and Bose-Einstein distributions, we can also consider distinguishable particle with degenerate energy levels, with no limit on the number of particles per energy state. Historically, this was the approach taken by Maxwell and Boltzmann in the classical era. As we will see, this can also be an excellent approximation to the B-E and F-D distributions under the right conditions.

The number of ways n_j distinguishable particles can be arranged among g_j states is

$$W_j = g_j^{n_j} \tag{5.16}$$

The total number of microstates due to the effects of degeneracy would then be

$$W_1 = \prod_j W_j$$

We must also consider the number of ways the distinguishable particles can be arranged among the energy levels, namely

$$W_2 = \frac{N!}{\prod_i n_j!} \tag{5.17}$$

Combining eq. (5.16) and eq. (5.17) gives the number of microstates per macrostate for M-B statistics as

$$W_{MB} = N! \prod_j \frac{g_j^{n_j}}{n_j!} \tag{5.18}$$

From this, it is easy to obtain the counterpart when the particles are indistinguishable, as these can be arranged $N!$ ways without changing the macrostate. As we will see shortly, this approximation to B-E and F-D statistics occurs in the dilute limit.

$$W_{DL} = \frac{W_{MB}}{N!} = \prod_j \frac{g_j^{n_j}}{n_j!} \tag{5.19}$$

Eq. (5.19) is referred to as corrected Maxwell-Boltzmann statistics.

5.7 Bose-Einstein Statistics

For a single energy level ε_j with degeneracy g_j. The number of microstates of n_j bosons is

$$W_j = \frac{(n_j + g_j - 1)!}{n_j! \, (g_j - 1)!} \tag{5.20}$$

Each energy level can be arranged independently, so that the total number of microstates for bosons in a given macrostate is

$$W_{BE} = \prod_j W_j = \prod_j \frac{(n_j + g_j - 1)!}{n_j! \, (g_j - 1)!} \tag{5.21}$$

Taking the natural logarithm of eq. (5.21), noting that $g_j \gg 1$, and applying Stirling's approximation gives

$$
\begin{aligned}
\ln W_{BE} &= \sum_j \left[\ln(n_j + g_j)! - \ln n_j! - \ln g_j! \right] \\
&= \sum_j \left[(n_j + g_j) \ln(n_j + g_j) - (n_j + g_j) - n_j \ln n_j + n_j - g_j \ln g_j + g_j \right] \\
&= \sum_i \left[n_j \ln \frac{g_j + n_j}{n_j} + g_j \ln \frac{g_j + n_j}{g_j} \right]
\end{aligned} \tag{5.22}
$$

5.8 Fermi-Dirac Statistics

For fermions, we can have at most one particle per degenerate state, so the number of microstates corresponding to n_j and g_j is given by

$$W_j = \frac{g_j!}{n_j!(g_j - n_j)!} \tag{5.23}$$

Again, each energy level is populated independently giving

$$W_{FD} = \prod_j W_j = \prod_j \frac{g_j!}{n_j!(g_j - n_j)!} \tag{5.24}$$

Taking logs, etc as before

$$\begin{aligned} \ln W_{FD} &= \sum_j \left[\ln g_j! - \ln n_j! - \ln(g_j - n_j)! \right] \\ &= \sum_j \left[g_j \ln g_j - g_j - n_j \ln n_j + n_j - (g_j - n_j)\ln(g_j - n_j) + g_j - n_j \right] \\ &= \sum_j \left[n_j \ln \frac{g_j - n_j}{n_j} - g_j \ln \frac{g_j - n_j}{g_j} \right] \end{aligned} \tag{5.25}$$

5.9   Combined B-E and F-D Notation

The similarity between eqs. (5.22) and (5.25) allows us to combine them as

$$\ln W = \sum_j \left[n_j \ln \frac{g_j \pm n_j}{n_j} \pm g_j \ln \frac{g_j \pm n_j}{g_j} \right] \tag{5.26}$$

where the top sign will always imply Bose-Einstein and the bottom Fermi-Dirac.

Lecture 6: The Partition Function

6.1   Most Probable Distribution

Now that we know the number of microstates for a given macrostate, we can find the most probable macrostate by differentiating eq. (5.26) to find the maximum, again with the constraints that

$$N = \sum_j n_j \qquad \text{and} \qquad E = \sum_j n_j \varepsilon_j$$

are both constant.

$$\begin{aligned} d\ln W &= d\sum_j \left[n_j \ln(g_j \pm n_j) - n_j \ln n_j \pm g_j \ln(g_j \pm n_j) \mp g_j \ln g_j \right] \\ &= \sum_j \left[\ln(g_j \pm n_j) \pm \frac{n_j}{g_j \pm n_j} - \ln n_j - 1 + \frac{g_j}{g_j \pm n_j} \right] dn_j \\ &= \sum_j \left[\ln(g_j \pm n_j) - \ln n_j \right] dn_j \end{aligned} \tag{6.1}$$

To identify the most probable macrostate, we must have

$$\sum_j \left[\ln(g_j \pm n_j) - \ln n_j \right] dn_j = 0 \tag{6.2}$$

For our isolated system, we again require the total number of particles and the total energy to remain constant.

$$\sum_j dn_j = 0 \qquad \sum_j \varepsilon_j dn_j = 0 \qquad (6.3)$$

Multiplying these two equations by Lagrange multipliers α and β and subtracting from eq. (6.2) gives

$$\sum_j \left[\ln(g_j \pm n_j) - \ln n_j - \alpha - \beta\varepsilon_j\right] dn_j = 0 \qquad (6.4)$$

For this to be generally true, we must have (as is common with Lagrange multipliers)

$$\ln \frac{g_j \pm n_j}{n_j} = \alpha + \beta\varepsilon_j \qquad (6.5)$$

Hence the most probable distribution among the energy levels is given by

$$n_j = \frac{g_j}{\exp(\alpha + \beta\varepsilon_j) \mp 1} \qquad (6.6)$$

This gives us two distributions, one for Bose-Einstein (-1) and one for Fermi-Dirac (+1). Next we must find the meaning of the Lagrange multipliers, α and β. To do this we turn again to entropy.

6.2 Entropy and the Lagrange Multipliers

We get W_{MP} when we put the equilibrium distribution of eq. (6.6) back into eq. (5.26). The first term in the summation is given directly by eq. (6.5). To get the second term, we manipulate eq. (6.5) and eq. (6.6).

$$\frac{g_j \pm n_j}{g_j} = \frac{g_j \pm n_j}{n_j} \frac{n_j}{g_j}$$
$$= \frac{\exp(\alpha + \beta\varepsilon_j)}{\exp(\alpha + \beta\varepsilon_j) \mp 1}$$
$$= \left[1 \mp \exp(-\alpha - \beta\varepsilon_j)\right]^{-1}$$

That is,

$$\ln W_{MP} = \sum_j \left[n_j(\alpha + \beta\varepsilon_j) \mp g_j \ln(1 \mp \exp(-\alpha - \beta\varepsilon_j))\right]$$
$$= \alpha N + \beta E \mp \sum_j \left[g_j \ln(1 \mp \exp(-\alpha - \beta\varepsilon_j))\right] \qquad (6.7)$$

From eq. (5.7), and noting $W_{MP} = W$ for large numbers,

$$S = k \ln W_{MP}$$

Therefore

$$S = k(\alpha N + \beta E) \mp k \sum g_j \ln(1 \mp \exp(-\alpha - \beta\varepsilon_j)) \qquad (6.8)$$

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To relate this to macroscopic thermodynamics, the classic analog is

$$dS(E, V, N) = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \tag{6.9}$$

where μ is the chemical potential. Depending on the context, the chemical potential can be included to allow for chemical changes, or ignored if these are irrelevant. We include it here for generality.

From eq.(6.8) and eq. (6.9), keeping V and N constant

$$\frac{\partial S}{\partial E} = k\beta = \frac{1}{T} \tag{6.10}$$

and keeping V and E constant

$$\frac{\partial S}{\partial N} = k\alpha = -\frac{\mu}{T} \tag{6.11}$$

Thus, the Lagrange multipliers are

$$\alpha = -\frac{\mu}{kT} \tag{6.12}$$

$$\beta = \frac{1}{kT} \tag{6.13}$$

Putting these back into eq. (6.8), we have

$$S = \frac{E - \mu N}{T} \mp k \sum_i g_i \ln \left(1 \mp \exp\left[-\frac{\varepsilon_j - \mu}{kT} \right] \right) \tag{6.14}$$

and the distribution is given from eq. (6.6)

$$n_i = \frac{g_i}{\exp\left[\frac{\varepsilon_i - \mu}{kT} \right] \mp 1} \tag{6.15}$$

6.3   Dilute Limit

If the number of particles is significantly less than the degeneracy of each energy level, the distinction between F-D and B-E statistics should disappear.

$$g_j \gg n_j \implies \text{dilute limit}$$

Accordingly, from eq. (5.26)

$$\ln W_{DL} = \sum_j \left[n_j \ln \frac{g_j}{n_j} \pm g_j \ln \left(1 \pm \frac{n_j}{g_j} \right) \right]$$

$$= \sum_j n_j \left(\ln \frac{g_j}{n_j} + 1 \right) \tag{6.16}$$

where we have made use of $\ln(1 + x) \to x$ as $x \to 0$.

Eq. (6.16) turns out to be identical to eq. (5.19) as can be shown by taking its natural log.

$$
\begin{aligned}
\ln W_{DL} &= \sum_j \ln \frac{g_j^{n_j}}{n_j!} \\
&= \sum_j \left[n_j \ln g_j - n_j \ln n_j + n_j \right] \\
&= \sum_j n_j \left(\ln \frac{g_j}{n_j} + 1 \right)
\end{aligned}
$$

So, in the dilute limit, the Bose-Einstein, Fermi-Dirac and corrected Maxwell-Boltzmann distributions are all the same. The particle distribution is given by

$$
n_j = g_j \exp\left(\frac{\mu - \varepsilon_j}{kT} \right) \tag{6.17}
$$

Note for $g_j \gg n_j$, we must have $\varepsilon_j \gg \mu$. That will likely be ok when $\mu < 0$, characteristic of ideal gases.

6.4   Partition Function

From eq. (6.17), we have

$$
n_j \exp\left(-\frac{\mu}{kT} \right) = g_j \exp\left(-\frac{\varepsilon_j}{kT} \right) \tag{6.18}
$$

Summing over j gives

$$
N e^{-\frac{\mu}{kT}} = Z \tag{6.19}
$$

where Z is called the molecular partition function

$$
Z = \sum_j g_j e^{-\frac{\varepsilon_j}{kT}} \tag{6.20}
$$

Alternatively, by summing over energy states,

$$
Z = \sum_i e^{-\frac{\varepsilon_i}{kT}} \tag{6.21}
$$

where each energy level has g_j terms of the same energy ε_j. i.e. $\varepsilon_i = g_j \varepsilon_j$. Eqs. (6.18) and (6.19) give

$$
n_j = \frac{N g_j \exp\left(-\frac{\varepsilon_j}{kT} \right)}{Z} \tag{6.22}
$$

Equivalently,

$$
n_i = \frac{N \exp\left(-\frac{\varepsilon_i}{kT} \right)}{Z} \tag{6.23}
$$

I am not enamoured by the term, partition function, but we seem to be stuck with it. The symbol, Z, comes from the German Zustandssumme, which means in this context sum-over-states, but can also mean partition. Seems lost in translation. Anyway, Z appears to be mainly a normalizing factor, summing over all energies for a given temperature. The distribution function, or real partitioning of N by energy level, is given by eq. (6.22) or eq. (6.23).

The relative population of state j, is thus

$$\frac{n_j}{N} = \frac{g_j \exp\left(-\frac{\varepsilon_j}{kT}\right)}{Z} \tag{6.24}$$

This works for both corrected and uncorrected M-B statistics, and is often simply called the Maxwell-Boltzmann distribution.

6.5 The Influence of Temperature

Firstly, we note that as $T \to \infty$,

$$Z \to \sum_j g_j$$

If we consider two different energy states, j and k,

$$\frac{n_j}{n_k} = \frac{g_j \exp\left(-\frac{\varepsilon_j}{kT}\right)}{g_k \exp\left(-\frac{\varepsilon_k}{kT}\right)} \tag{6.25}$$

or

$$\frac{n_j g_k}{n_k g_j} = \exp\left(-\frac{\varepsilon_j - \varepsilon_k}{kT}\right) \tag{6.26}$$

Then

$$\lim_{T \to 0}\left(\frac{n_j g_k}{n_k g_j}\right) = 0 \qquad \lim_{T \to \infty}\left(\frac{n_j g_k}{n_k g_j}\right) = 1$$

As T increases, the distribution moves from one dominated by lower energy levels, to random distribution across all energy levels.

In thermodynamic equilibrium, if each energy level has only a single state ($g = 1$), eq. (6.23) tells us that the population of any excited energy state can never exceed that of the ground state (or less excited state).

If we encounter a contrary situation, termed a population inversion, then this implies the system is not in thermodynamic equilibrium. To revert to equilibrium we must lose relative numbers from the higher energy states, typically by collision or radiation.

Again, as $T \to 0$, in equilibrium we must have $E \to N\varepsilon_0$, with all particles in the ground state.

Lecture 7: Partition Functions and Thermodynamic Properties in the Dilute Limit

7.1 The Dilute Limit (again)

We had earlier that this occurs when $g_j \gg n_j$ for all j.

From eq. (6.17), this also means

$$\exp\left(\frac{\varepsilon_j - \mu}{kT}\right) \gg 1 \tag{7.1}$$

This will be guaranteed whenever $\exp\left(-\frac{\mu}{kT}\right) \gg 1$, or from eq. (6.19) whenever

$$\frac{Z}{N} \gg 1 \tag{7.2}$$

7.2 Internal Energy and Entropy

We had

$$U = E = \sum_j n_j \varepsilon_j \tag{7.3}$$

From eq. (6.24)

$$U = \frac{N}{Z} \sum g_j \varepsilon_j e^{-\frac{\varepsilon_j}{kT}} \tag{7.4}$$

From eq. (6.20)

$$\frac{\partial Z}{\partial T} = \frac{1}{kT^2} \sum_j g_j \varepsilon_j e^{-\frac{\varepsilon_j}{kT}} \tag{7.5}$$

From which

$$U = \frac{NkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right) = NkT^2 \left(\frac{\partial \ln Z}{\partial T}\right) \tag{7.6}$$

Stealing a result from quantum mechanics, the energy levels are a function only of the volume of the particle assembly. Hence $Z = Z(T, V)$ (so the above partial derivatives must be at constant volume). Also $U = U(T, V, N)$.

Turning to entropy, we had from eq. (6.14)

$$S = \frac{E - \mu N}{T} \mp k \sum_i g_i \ln\left(1 \mp \exp\left[-\frac{\varepsilon_j - \mu}{kT}\right]\right)$$

In the dilute limit, the summation term becomes

$$\mp k \sum_i g_i \ln\left(1 \mp \exp\left[-\frac{\varepsilon_j - \mu}{kT}\right]\right) \approx \mp k \sum_i g_i \left[\mp \exp\left[-\frac{\varepsilon_j - \mu}{kT}\right]\right]$$

$$= k \sum_i g_i \exp\left[\frac{\mu - \varepsilon_j}{kT}\right]$$

$$= k e^{\frac{\mu}{kT}} Z$$

$$= kN$$

That is,

$$S = \frac{U}{T} + kN\left(1 - \frac{\mu}{kT}\right) \tag{7.7}$$

Or, from eq. (6.19)

$$S = \frac{U}{T} + kN\left(\ln \frac{Z}{N} + 1\right) \tag{7.8}$$

Or, all in terms of N and Z,

$$S = Nk\left(T\left(\frac{\partial \ln Z}{\partial T}\right) + \ln \frac{Z}{N} + 1\right) \tag{7.9}$$

So $S = S(T, V, N)$, just as U.

And the dilute limit means this applies equally to MB, BE and FD particles.

Going back to the definition of eq. (5.19) we can also write

$$\ln W_{DL} = \ln W_{MB} - \ln N!$$

$$= \ln W_{MB} - N(\ln N - 1) \tag{7.10}$$

So that

$$S_{MB} = S_{DL} + kN(\ln N - 1) \tag{7.11}$$

and for distinguishable particles, eqs. (7.8) and (7.11) give

$$S = \frac{U}{T} + kN \ln Z \tag{7.12}$$

7.3   Other Thermodynamic Properties

Laurendeau 4.5

From eq. (6.19)

$$\mu = -kT \ln \frac{Z}{N} \tag{7.13}$$

The Gibbs free energy,

$$G = \mu N = -NkT \ln \frac{Z}{N} \tag{7.14}$$

Also, $G = H - TS$, so that

$$
\begin{aligned}
H &= -NkT \ln \frac{Z}{N} + U + NkT \left(\ln \frac{Z}{N} + 1 \right) \\
&= NkT \left(T \frac{\partial \ln Z}{\partial T} + 1 \right)
\end{aligned} \tag{7.15}
$$

And since $H = U + pV$,

$$pV = NkT \tag{7.16}$$

This of course is also the equation of state for an ideal gas. We get this because ideal gas behaves like independent but indistinguishable particles in the dilute limit, and ideal gases typically have large negative chemical potentials.

This result also allows us to connect k to the universal gas constant R^*, by comparing with the macroscopic result

$$pV = nR^*T \tag{7.17}$$

where here n is the number of moles, $n = \frac{N}{N_A}$, with N_A being Avogadro's number. That is,

$$k = \frac{nR^*}{N} = \frac{R^*}{N_A} \tag{7.18}$$

We can also get the macroscopic heat capacities

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = Nk \left[\frac{\partial}{\partial T} T^2 \left(\frac{\partial \ln Z}{\partial T} \right) \right]_V \tag{7.19}$$

$$
\begin{aligned}
C_P &= \left(\frac{\partial H}{\partial T} \right)_P \\
&= \left(\frac{\partial H}{\partial T} \right)_V \\
&= Nk \left[\left(\frac{\partial}{\partial T} T^2 \frac{\partial \ln Z}{\partial T} \right)_V + 1 \right]
\end{aligned} \tag{7.20}
$$

since for an ideal gas H is only a function of T.

7.4 Summary of Intensive Thermodynamic Properties

These can be expressed dimensionlessly, using lower case to distinguish the molar quantities (watch out for g, here being the molar amount of Gibbs free energy, not degeneracy).

Internal Energy

$$\frac{u}{R^*T} = T\left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{7.21}$$

Enthalpy

$$\frac{h}{R^*T} = T\left(\frac{\partial \ln Z}{\partial T}\right)_V + 1 \tag{7.22}$$

Entropy

$$\frac{s}{R^*} = T\left(\frac{\partial \ln Z}{\partial T}\right)_V + \ln\frac{Z}{N} + 1 \tag{7.23}$$

Gibbs

$$\frac{g}{R^*T} = -\ln\frac{Z}{N} \tag{7.24}$$

Helmholtz

$$\frac{a}{R^*T} = -\left(\ln\frac{Z}{N} + 1\right) \tag{7.25}$$

Specific heat at constant volume

$$\frac{c_V}{R^*} = \left(\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z}{\partial T}\right)\right)_V \tag{7.26}$$

Specific heat at constant pressure

$$\frac{c_P}{R^*} = \left(\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z}{\partial T}\right)\right)_V + 1 \tag{7.27}$$

Knowing Z and its dependence on T, and sometimes N, is all it takes!

We need to know $\ln\left(\frac{Z}{N}\right)$, $\left(\frac{\partial \ln Z}{\partial T}\right)_V$ and $\left(\frac{\partial^2 \ln Z}{\partial T^2}\right)_V$.

for this we need to know the degeneracies, g_j, and the energy levels, ε_j, for the atoms or molecules making up our system.

7.5 Example

Laurendeau example 4.1

Consider a dilute system in thermodynamic equilibrium with 50 independent, indistinguishable particles. Each particle can be in one of 3 energy states: $0, \varepsilon$, and 2ε, with degeneracies of 300, 600 and 1200, respectively. The system is at a constant $T = \frac{\varepsilon}{k}$.

(a) What is Z for this system?

$$Z = \sum_{j=0}^{2} g_j e^{-\frac{\varepsilon_j}{kT}} = 300e^0 + 600e^{-1} + 1200e^{-2} \approx 683$$

(b) How many particles are in each energy level?

$$n_0 = \frac{N g_0 e^0}{Z} = \frac{50 \times 300}{683} \approx 22$$

$$n_1 = \frac{50 \times 600 e^{-1}}{683} \approx 16$$

$$n_2 = \frac{50 \times 1200 e^{-2}}{683} \approx 12$$

(c) Determine the entropy of this system from Boltzmann's relation.

$$S = k \ln W_{DL} = k \sum_{j=0}^{2} n_j \left[\ln \frac{g_j}{n_j} + 1 \right]$$

$$= k \left[22 \left[\ln \left(\frac{300}{22} \right) + 1 \right] + 16 \left[\ln \left(\frac{600}{16} \right) + 1 \right] + 12 \left[\ln \left(\frac{1200}{12} \right) + 1 \right] \right]$$

$$\approx 221k$$

(d) Determine the internal energy of this system.

$$U = \sum_{j=0}^{2} n_j \varepsilon_j = 22 \times 0 + 16 \times \varepsilon + 12 \times 2\varepsilon = 40\varepsilon$$

(e) Calculate the entropy directly from the partition function.

$$S = \frac{U}{T} + kN \left[\ln \frac{Z}{N} + 1 \right] = 40k + 50k \left[\ln \frac{683}{50} + 1 \right] = 221k$$

(f) Calculate the Gibbs free energy.

$$G = -NkT \ln \frac{Z}{N} = -50\varepsilon \ln \frac{683}{50} = -131\varepsilon$$

Lecture 8: Z for Translational Energy in an Ideal Gas

8.1 Translational Modes of an Ideal Gas

Laurendeau 5.7

This is a repeat of kinetic theory in our context. We consider the translational kinetic energy of the atoms or molecules of a gas, behaving as though it were ideal (no van der Waals considerations).

To obtain the energy levels available to an atom or molecule, we have to dip into quantum mechanics just far enough to note that in the limit of really small quantities, the energy, momentum, position, etc. of an atom or molecule cannot be known with infinite precision, but are quantized, and affected by the uncertainty principle. For example, a single free particle of mass m, constrained to traverse a cubical box of dimension L, will be governed by a wave function

$$\Psi = \left(\frac{8}{L^3}\right)^{1/2} \sin\left(\frac{n_1 \pi x}{L}\right) \sin\left(\frac{n_2 \pi y}{L}\right) \sin\left(\frac{n_3 \pi z}{L}\right) \tag{8.1}$$

This is where the three quantum numbers, n_1, n_2, n_3 originate. By evaluating the energy associated with the wave function, the total translational energy of thep article is found to be

$$\varepsilon_{tr} = \frac{h^2}{8mV^{2/3}}\left(n_1^2 + n_2^2 + n_3^2\right) \tag{8.2}$$

where h is Planck's constant, $V = L^3$ and n_x are quantum numbers for each of the three degrees of translational freedom.

We can deduce a lot from eq. (8.2).

1. The proportionality to h^2 means very small separation between energy levels – too small to be detectable spectroscopically. To all practical purposes we can regard the translational energy in finite volumes as being continuous.

2. The energy does depend on volume; hence the assumptions in the previous lecture that changes were taking place at constant volume.

3. There are multiple combinations of quantum numbers that will give the same energy, providing a degeneracy that generally increases with energy.

4. Since each of the quantum numbers can range from 1 to ∞, the number of possible energy states is unlimited, meaning that most are unoccupied. To show this we consider the density of translational energy states.

8.2 Density of Translational Energy States

The separation of energy states is so small that we can consider the energy as being continuously distributed, with a pdf that depends on $n = \left(n_1^2 + n_2^2 + n_3^2\right)^{1/2}$. The number of states having energy $\varepsilon \leq \varepsilon_{tr}$ is the volume in quantum number space (imagine Cartesian axes for the three quantum numbers) occupied by the positive octant of a sphere of radius n. Denote this by M_ε

$$
\begin{aligned}
M_\varepsilon &= \frac{1}{8}\frac{4\pi n^3}{3} \\
&= \frac{\pi}{6}\left[\frac{8mV^{2/3}\varepsilon_{tr}}{h^2}\right]^{3/2} \\
&= \frac{4\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2} V\varepsilon_{tr}^{3/2}
\end{aligned}
\tag{8.3}
$$

Differentiating gives the pdf, or density of states as

$$
D(\varepsilon_{tr})d\varepsilon_{tr} = 2\pi\left(\frac{2m}{h^2}\right)^{3/2} V\varepsilon_{tr}^{1/2}d\varepsilon_{tr}
\tag{8.4}
$$

Example. Consider 1cm^3 of H$_2$ at 298K, and at 1atm. From the ideal gas law this implies 2.5×10^{19} molecules. From eq. (8.3) we would find that $M_\varepsilon = 4 \times 10^{24}$, implying O($10^5$) available states per molecule. As a result, we can be confident that for most situations, any gas will satisfy the dilute limit. (Consider what conditions would be needed for this not to be true.)

8.3 Z_{tr} for a Monatomic Gas

For convenience in what will follow, we sometimes express the energy in terms of wave number, and in terms of temperature.

That is,

$$
\tilde{\varepsilon} = \frac{\varepsilon}{hc}
\tag{8.5}
$$

with units of cm^{-1}.

Defining

$$
\alpha_{tr} = \frac{h}{8mcV^{2/3}}
\tag{8.6}
$$

the translational energy eq. (8.2) can be written

$$
\tilde{\varepsilon}_{tr} = \alpha_{tr}\left(n_1^2 + n_2^2 + n_3^2\right)
\tag{8.7}
$$

And to relate this to temperature, θ, we note

$$\theta = \frac{\varepsilon}{k} = \frac{hc}{k}\tilde{\varepsilon} = 1.4387\tilde{\varepsilon} \tag{8.8}$$

where $\tilde{\varepsilon}$ is in cm^{-1}, and θ in in K.

We then define the characteristic translational temperature as

$$\theta_t = \frac{hc}{k}\alpha_{tr} = \frac{h^2}{8mkV^{2/3}} \tag{8.9}$$

e.g. For 1 cm^3 of H$_2$, $\theta_t \sim 10^{16}$ K.

The very low value of θ_t is also consistent with the result of section 8.2.

Directly from eq. (8.2) we can sum over all energy states to obtain

$$\begin{aligned} Z_{tr} &= \sum_{n_1=1}^{\infty}\sum_{n_2=1}^{\infty}\sum_{n_3=1}^{\infty} \exp\left[-\frac{h^2}{8mV^{2/3}kT}\left(n_1^2 + n_2^2 + n_3^2\right)\right] \\ &= \left[\sum_{n=1}^{\infty}\exp\left(-\frac{\theta_t n^2}{T}\right)\right]^3 \end{aligned} \tag{8.10}$$

Z_{tr} is usually very large. So large that we can replace the summation of eq. (8.10) by an integral.

$$Z_{tr} = \left[\int_0^{\infty}\exp\left(-\frac{\theta_t n^2}{T}\right)dn\right]^3 = \left[\frac{1}{2}\sqrt{\frac{\pi T}{\theta_t}}\right]^3 \tag{8.11}$$

(using tables of integrals), or

$$Z_{tr} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2}V \tag{8.12}$$

This is consistent with what we got from classical considerations using the equipartition of energy – a result allowable by the extremely large numbers of very closely spaced energy levels.

Example. Find the ratio of $\frac{Z_{tr}}{N}$ for molecular nitrogen at 300 K and 1 atm. $\sim 2 \times 10^6$.

8.4 Z_{tr} and the Thermodynamic Properties of a Monatomic Gas

From eq. (8.12) we find

$$T\left(\frac{\partial \ln Z}{\partial T}\right)_V = T\frac{\partial}{\partial T}\left(\frac{3}{2}\ln\frac{2\pi mk}{h^2} + \frac{3}{2}\ln T + \ln V\right)_V = \frac{3}{2} \tag{8.13}$$

and

$$\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{3}{2}\frac{\partial}{\partial T}T = \frac{3}{2} \tag{8.14}$$

We already had

$$\frac{u}{R^*T} = T\left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{8.15}$$

So the internal energy is given by

$$\left(\frac{u}{R^*T}\right)_{tr} = \frac{3}{2} \tag{8.16}$$

Similarly,

$$\left(\frac{c_V}{R^*}\right)_{tr} = \frac{3}{2} \qquad \left(\frac{h}{R^*T}\right)_{tr} = \frac{5}{2} \qquad \frac{c_P}{R^*} = \frac{5}{2}$$

To find pressure, we note that it is related to the Helmholtz free energy

$$-P = \left(\frac{\partial A}{\partial V}\right)_{T,N} \tag{8.17}$$

and A is given by

$$A = -NkT\left[\ln\frac{Z}{N} + 1\right] \tag{8.18}$$

Because $Z = Z(T, V)$,

$$\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N} = \frac{1}{V}$$

and so

$$P = NkT\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{NkT}{V} \tag{8.19}$$

telling us that pressure arises solely from the translational mode. It also tells us that any non-translational forms of internal energy must not be dependent on volume, just on temperature.

8.5 Sackur-Tetrode Equation

We also had entropy as

$$\frac{s}{R^*} = T\left(\frac{\partial \ln Z}{\partial T}\right)_V + \ln\frac{Z}{N} + 1 \tag{8.20}$$

so that

$$\left(\frac{s}{R^*}\right)_{tr} = \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \ln\frac{V}{N} + \frac{5}{2} \tag{8.21}$$

and from eq. (8.19),

$$\left(\frac{s}{R^*}\right)_{tr} = \ln\left[\frac{(2\pi m)^{3/2}(kT)^{5/2}}{h^3 P}\right] + \frac{5}{2} \tag{8.22}$$

Writing M for the molecular weight (kg/kmole), with P in bars, this can be written as the Sackur-Tetrode equation

$$\left(\frac{s}{R^*}\right)_{tr} = \frac{5}{2}\ln T + \frac{3}{2}\ln M - \ln P - 1.1516 \tag{8.23}$$

This only applies in the dilute limit.

8.6 Example

Determine the contribution to the Helmholtz free energy (kJ/mole) from the translational energy mode at 500 K and 2 bars for monatomic helium.
We seek

$$\left(\frac{a}{RT}\right)_{tr} = -\left[\ln\left(\frac{Z_{tr}}{N}\right) + 1\right]$$

From eqs. (8.12) and (8.19), we have

$$\frac{Z_{tr}}{N} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2}\left(\frac{kT}{P}\right)$$

which evaluates to $\frac{Z_{tr}}{N} = 5.808 \times 10^5$ and $\left(\frac{a}{RT}\right)_{tr} = -14.272$.

So that $a_{tr} = -58.333$ kJ/mole

Lecture 9: More on Z

9.1 Symmetric and Antisymmetric Wave Functions

Laurendeau 5.9, 5.10

Dipping back briefly into quantum mechanics, we comment further on the nature of particles. Classical particles are distinguishable because, in principle, the identity of individual particle trajectories in phase space can be followed. At the quantum mechanical level, where particles exist by virtue of their wave function, which is essentially a probability distribution, the path of one particle cannot be distinguished from another, so the particles are indistinguishable, which is what we assumed for the B-E and F-D statistics earlier. This leads to natural symmetry conditions for the wave function of any multi-particle system.

We must be able to interchange particles without affecting an observable outcome. In quantum mechanical language this means that $\Psi(r_1, r_2, r_3...r_N)$ must give the same $\Psi^*\Psi$ if we interchange any of the particles. This will be satisfied if the wave function is such that

$$\Psi(r_1, r_2, r_3...r_N) = \pm\Psi(r_2, r_1, r_3, ...r_N) \tag{9.1}$$

That is, the wave function must be symmetric (+) or antisymmetric (-) with respect to the exchange of any two of its particles.

Elementary particles with symmetric wave functions are called bosons, and these include photons, and nuclei with even mass number. Bosons have integral spin quantum numbers (we may need this later), and are not affected by the Pauli exclusion principle.

Elementary particles with antisymmetric wave functions are called fermions, and these include electrons, protons, neutrons, and nuclei with odd mass number. Fermions have half-integral spin quantum numbers, and are affected by the Pauli exclusion principle.

For example, consider the wave function of two particles expressed as

$$\Psi(r_1, r_2) = \Psi_i(r_1)\Psi_j(r_2) \pm \Psi_i(r_2)\Psi_j(r_1) \tag{9.2}$$

where the notation $\Psi_j(r_k)$ means that particle r_k is in quantum state j, etc. The $\pm$ sign determines whether $\Psi(r_1, r_2)$ is symmetric or antisymmetric. Further, by setting $i = j$ we see that for the symmetric version

$$\Psi(r_1, r_2) = \Psi_i(r_1)\Psi_i(r_2) + \Psi_i(r_2)\Psi_i(r_1) = 2\Psi_i(r_1)\Psi_i(r_2) \tag{9.3}$$

whereas for the antisymmetric version

$$\Psi(r_1, r_2) = \Psi_i(r_1)\Psi_i(r_2) - \Psi_i(r_2)\Psi_i(r_1) = 0 \tag{9.4}$$

This means there is no probability of finding two like particles with antisymmetric wave functions in the same quantum state in the same multi-particle system, which is where the Pauli exclusion principle comes from. So we get at most one fermion with each unique set of quantum numbers, and no limit to the number of bosons with same quantum numbers.

9.1.1 Bosons and Fermions

Laurendeau 5.10

(a) Bosons
Have symmetric wave functions and do not follow the Pauli exclusion principle. Use Bose-Einstein statistics. Examples include photons, phonons and nuclei of even mass number (protons+neutrons in the nucleus). They have an integral spin quantum number.

(b) Fermions
Have antisymmetric wave functions and follow the Pauli exclusion principle. Use Fermi-Dirac statistics. Examples include electrons, protons, neutrons, nuclei with odd mass numbers. Have half-integral spin quantum numbers.

9.2 External and Internal Modes of Energy

Laurendeau 8.2

Considering a single particle system such as a monatomic gas, we note the particle can have both external and internal modes of energy. The external mode is always present in terms of translational energy. As we have noted, while there is a quantum mechanical basis even for translational energy, the quantum numbers are so numerous and closely spaced that the behaviour of the translational mode is quite classical. Not so for the internal modes. A monatomic gas can have an electronic mode of internal energy, and once we move to diatomic molecules the additional internal modes of rotational and vibrational energy become possible.

9.2.1 Internal Energy for Atoms and Diatomic Molecules

For atoms, we can ignore the vibrational and rotational energies, and just have the electronic energy, ε_{el}, which will be quantized, but gets quite complicated for arbitrary atoms.

$$\varepsilon_{tot} = \varepsilon_{tr} + \varepsilon_{el} \tag{9.5}$$

For diatomic and polyatomic molecules, we also have the rotational and vibrational energies

$$\varepsilon_{tot} = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{el} \tag{9.6}$$

The different energies each have their own degeneracies, expressible in general as

$$g = g_{tr}g_{rot}g_{vib}g_{el} \tag{9.7}$$

Getting to this state of simple identification, without coupling between the types of energy is an approximation that makes use of the harmonic-oscillator model, the rigid-rotor assumption, and the Born-Oppenheimer approximation.

Given the constants involved, we often simply refer to the energy by its wave number, $\tilde{\nu} = \frac{1}{\lambda}$.

That is, $\varepsilon = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}$, or $\tilde{\nu} = \frac{\varepsilon}{hc}$, usually expressed in units of cm^{-1}.

Similarly, for each type of energy it is also convenient to be able to express these also in terms of temperatures, noting that kT has units of energy. That is,

$$T = \frac{\varepsilon}{k} = \frac{hc\tilde{\nu}}{k} = (1.4387 \text{ cm K})\tilde{\nu}$$

We can define characteristic temperatures for each type of energy: $\theta_{tr}, \theta_r, \theta_\nu, \theta_e$. These in turn can be written as

$$\theta_{tr} = \frac{hc}{k}\alpha_{tr} \qquad \theta_r = \frac{hc}{k}B_e \qquad \theta_\nu = \frac{hc}{k}\omega_e \qquad \theta_e = \frac{hc}{k}T_e \tag{9.8}$$

where the multipliers are constants of the system in wave number units.

e.g. For 1 cm^3 of molecular H_2, the characteristic translational, rotational, vibrational and electronic temperatures are, respectively: 10^{-16} K, 10 K, 10^3 K and 10^5 K.

9.2.2 Rotational Energy

Considering a diatomic molecule as a rigid rotator leads to a quantized energy of rotation of the form

$$\varepsilon_{rot} = \frac{J(J+1)\hbar^2}{2I} \tag{9.9}$$

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where I is the moment of inertia of the molecule, and J is the rotational quantum number.

Writing the constant component of this as

$$B_e = \frac{h}{8\pi^2 c I_e} \tag{9.10}$$

where the e subscript implies the moment of inertia is at the equilibrium internuclear distance, and using wave number units for convenience, we have

$$F(J) = \frac{\varepsilon_{rot}}{hc} = J(J+1)B_e \tag{9.11}$$

where $J = 0, 1, 2...$

For any J, there are additional states specified by the magnetic quantum number m, where

$$m = 0, \pm 1, \pm 2, ..., \pm J \tag{9.12}$$

The effect of m can be observed when there is a magnetic field (the Zeeman effect). As a result each rotational energy level specified by J has a degeneracy of $g_{rot} = 2J + 1$.

9.2.3 Vibrational Energy

Laurendeau 6.4, 9.2.5

Quantum considerations again lead to discrete energy levels for the vibrational energy of a molecule.

$$\varepsilon_{vib} = (v + \frac{1}{2})h\nu \tag{9.13}$$

where v is the vibrational quantum number. Note that in the ground state, where $v = 0$, the vibrational energy does not vanish. This non-zero energy ground state of $\varepsilon_0 = \frac{1}{2}h\nu$ is a consequence of Heisenberg's uncertainty principle.

The total energy of a harmonic oscillator has kinetic and potential contributions, giving

$$\varepsilon_{vib} = \left(\frac{p^2}{2\mu}\right) + \left(\frac{k_0 x^2}{2}\right) \tag{9.14}$$

where p is the momentum, μ is the reduced mass, k_0 the restoring force and x the displacement. The point being that we can't have both velocity and position zero at the same time.

Converting to wave number units as before, we have

$$G(v) = \frac{\varepsilon_{vib}}{hc} = \left(v + \frac{1}{2}\right)\omega_e \tag{9.15}$$

where the vibrational frequency (cm^{-1}) can be defined as

$$\omega_e = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k_0}{\mu}} \tag{9.16}$$

For the vibrational mode, there is no degeneracy, and $g_{vib} = 1$ for all v.

Equations (9.11) and (9.15) are useful approximations for the rotational and vibrational energies of a diatomic molecule. They are derived assuming a rigid rotator, with small vibrational perturbations about its equilibrium position.

9.2.4 Electronic Energy

Tricky. For now, we specify by T_e, and note that there will be degeneracies. The electronic modes are triggered at high temperatures, and for many problems may not be needed.

9.2.5 Total Internal Energy

$$\varepsilon_{int} = \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{el} \tag{9.17}$$

In wave number units

$$\begin{aligned}
\tilde{\varepsilon} &= F(J) + G(v) + T_e \\
&= J(J+1)B_e + \left(v + \frac{1}{2}\right)\omega_e + T_e
\end{aligned} \tag{9.18}$$

Because of the difference in characteristic temperatures, we always have

$$\Delta\varepsilon_{rot} < \Delta\varepsilon_{vib} < \Delta\varepsilon_{el} \tag{9.19}$$

Lecture 10: Rotational Energies

10.1 Rigid Diatomic Molecules

Laurendeau 6.3

Considering a diatomic molecule as a rigid rotator with atoms of m_1 and m_2 separated by r, leads to a moment of inertia,

$$I = \frac{m_1 m_2}{m_1 + m_2}r^2 = \mu r^2 \tag{10.1}$$

where μ is called the reduced mass. The angular momentum is $I\omega$ and the kinetic energy of rotation

$$\varepsilon_{rot} = \frac{1}{2}I\omega^2 = \frac{(I\omega)^2}{2I} \tag{10.2}$$

From quantum mechanics, we find the angular momentum is quantized,

$$I\omega = \frac{h}{2\pi}\left[J(J+1)\right]^{1/2} \tag{10.3}$$

where J is the rotational quantum number. The energy is also quantized,

$$\varepsilon_{rot} = \frac{J(J+1)\hbar^2}{2I} \tag{10.4}$$

Writing the constant component of this as

$$B_e = \frac{h}{8\pi^2 c I_e} \tag{10.5}$$

where the e subscript implies the moment of inertia is at the equilibrium internuclear distance, and using wave number units for convenience, we have

$$F(J) = \frac{\varepsilon_{rot}}{hc} = J(J+1)B_e \tag{10.6}$$

where $J = 0, 1, 2, ...$

10.2 Molecules in General

For any molecule to have pure rotational internal energy, it must have a permanent electric dipole moment. This implies some sort of charge asymmetry. Diatomic molecules with atoms from different elements (heteronuclear), such as CO, have permanent dipole moments, whereas homonuclear molecules, such as O_2, do not. Neither do linear symmetric polyatomic molecules such as CO_2 or some other symmetric molecules, such as CH_4. Asymmetric linear molecules, such as N_2O, and bent molecules, such as H_2O and O_3 have permanent dipole moments. For those molecules that do not have permanent moments, however, once they start to vibrate they may develop a dipole moment that allows them to couple with the electromagnetic field and rotate.

The considerations of the previous section apply to more general molecules provided we can use more rotational constants, corresponding the moments of inertia about all the relevant axes. Thus linear molecules just need B, whereas asymmetric tops (e.g. bent triatomic molecules such as H_2O and 0_3) have a different rotational constant for each rotational degree of freedom, A, B, and C.

10.3 Rotational Transitions

Laurendeau 7.1

Given the quantization of the rotational energy levels, transitions from one to another absorb or emit discrete quanta of radiant energy. The selection rules for these transitions, in the rigid rotator quantum model are

$$\Delta J = \pm 1 \tag{10.7}$$

By convention, we introduce a primed notation, whereby ε'' always refers to the lower energy state of the transition, and ε' refers to the upper state. Thus for rotational transitions

$$J' - J'' \equiv 1 \tag{10.8}$$

and

$$\Delta\tilde{\varepsilon} = \tilde{\varepsilon}' - \tilde{\varepsilon}'' = \Delta F(J) = \left[J'\left(J'+1\right) - J''\left(J''+1\right) \right] B = 2J'B \tag{10.9}$$

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Thus if we look at a rotational spectrum in wave number units, we would expect to see lines that are equally spaced by $2B$ cm^{-1}.

Example. Carbon Monoxide CO
Mass of ^{12}C=1.99$\times$10^{-26} kg
Mass of ^{16}O=2.66 $\times$ 10^{-26} kg
Internuclear spacing of CO=0.113 nm
Therefore, $\mu = 1.14 \times 10^{-23}$ g, $I = 1.46 \times 10^{-46}$ kg m^2 and $B_e = 192$ cm$^{-1} = 1.92$ m^{-1}, corresponding to a wavelength of 5 mm, and the rotational lines would be spaced apart by 3.84 cm^{-1}.

Note the power of using spectroscopy to determine molecular configurations. By measuring the line spacing of the rotational lines, the rotational constant is measured, and from this the moment of inertia, and thus the internuclear distances (if the mass is known). For asymmetric top molecules, such as H$_2$0, knowledge of I also allows the bond angle to be calculated.

For a rigid rotator, as we have discussed, the line spacings are equal. In practice, as J increases centrifugal stretching increases the moment of inertia, and reduces the rotational constant, so that the lines get slightly closer together.

10.4 Rotational Degeneracy

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Directly from the quantum mechanics, there are multiple solutions of the rotational wave equation for given J. These are specified by the so-called magnetic quantum number m, such that $|m| \leq J$. Physically, one can image an applied electric field, the angular momentum vector, $\boldsymbol{J}$, tries to align with this field, either parallel or antiparallel, but cannot, and instead precesses around the electric field vector, much as a gyroscope precesses around the gravity vector. The component of $\boldsymbol{J}$ parallel to the electric field must be quantized and an integer multiple of $\frac{h}{2\pi}$. That is, the angles that $\boldsymbol{J}$ makes with the electric field are also quantized.

Some thought shows that the number of possible angles $= 2J + 1$. All of these states have equal probabilities of occurrence. These states are explicit in the presence of an electric field and become implicit as the field is reduced to zero. For now, we can simply summarize this as saying for rotational quantum number J, there are $2J + 1$ degenerate states, giving this energy level a comparable statistical weight of $2J + 1$.

$$g_{rot} = 2J + 1 \tag{10.10}$$

10.5 Rotational Partition Function

In the dilute limit, we found that all thermodynamic properties were related to $\ln Z$. This allows us to simply add the contributions from each energy mode. For example,

$$Z = \sum_j g_j e^{-\frac{\varepsilon_j}{kT}} = \sum g_{tr,k} g_{int,l} \exp\left[-\frac{\varepsilon_{tr,k} + \varepsilon_{int,l}}{kT}\right] \tag{10.11}$$

can be written

$$Z = \left[\sum_k g_{tr,k} e^{-\frac{\varepsilon_{tr,k}}{kT}} \right] \left[\sum_l g_{int,l} e^{-\frac{\varepsilon_{int,l}}{kT}} \right] = Z_{tr} Z_{int} \qquad (10.12)$$

and the internal energy can similarly be broken down into its rotational, vibrational and electronic components, so that

$$\ln Z = \ln Z_{tr} + \ln Z_{rot} + \ln Z_{vib} + \ln Z_{el} \qquad (10.13)$$

This in turn allows us to break down the various thermodynamic properties into their individual components due to each of the energy modes.

Accordingly, for rotational energy modes, we have

$$Z_{rot} = \sum_J g_J e^{-\frac{\varepsilon_{rot,J}}{kT}} = \sum_J (2J+1) \exp \left[\frac{-J(J+1)\theta_r}{T} \right] \qquad (10.14)$$

where we have used the characteristic rotational temperature again

$$\theta_r = \frac{hc}{k} B_e = \frac{h^2}{8\pi^2 k I_e}$$

This is ok for heteronuclear diatomic molecules, and asymmetric polyatomic molecules, but needs to be corrected if the molecular symmetry creates indistinguishable configurations. For this correction we introduce a symmetry factor, σ, and write a corrected version of eq. (10.14) as

$$Z_{rot} = \frac{1}{\sigma} \sum_J (2J+1) \exp \left[\frac{-J(J+1)\theta_r}{T} \right] \qquad (10.15)$$

where $\sigma = 2$ if symmetry creates an indistinguishable arrangement, as for homonuclear diatomic molecules such as 0_2 (which don't have a permanent dipole moment anyway); otherwise $\sigma = 1$.

Eq. (10.15) can be evaluated numerically. But there are also some good analytic approximations, depending on the value of $\frac{\theta_r}{T}$.

At low temperatures, where $T \leq 3\theta_r$, we have to evaluate eq. (10.15) numerically.

For larger temperatures, $3\theta_r < T < 30\theta_r$, we can apply an Euler-Maclaurin expansion

$$Z_{rot} = \frac{T}{\sigma \theta_r} \left[1 + \frac{1}{3} \left(\frac{\theta_r}{T} \right) + \frac{1}{15} \left(\frac{\theta_r}{T} \right)^2 + \frac{4}{315} \left(\frac{\theta_r}{T} \right)^3 + ... \right] \qquad (10.16)$$

For $T \gg \theta_r$ this simplifies further to

$$Z_{rot} = \frac{T}{\sigma \theta_r} \qquad (10.17)$$

For this last case, we easily have

$$T \left(\frac{\partial \ln Z_{rot}}{\partial T} \right)_V = 1$$

This leads to

$$\left(\frac{u}{R^* T} \right)_{rot} = 1 \qquad \left(\frac{c_v}{R^*} \right)_{rot} = 1$$

10.6   Rotational Populations

From eq. (10.14) we can examine the relative population of rotational states for given T. For example, taking a heteronuclear diatomic molecule, we have

$$\frac{N_J}{N} = \frac{g_J e^{-\frac{\varepsilon_J}{kT}}}{Z_{rot}} = \frac{2J+1}{Z_{rot}} \exp \left[-\frac{J(J+1)\theta_r}{T} \right] \qquad (10.18)$$

Relative to the ground state, we have

$$\frac{N_J}{N_0} = (2J+1) \exp \left[-\frac{J(J+1)\theta_r}{T} \right] \qquad (10.19)$$

What is interesting about this is that the peak in the distribution need not occur at the ground state, but somewhat above it, due to the effect of increasing degeneracy with J. If we treat the distribution as continuous in J, for example, and differentiate eq. (10.19) to find the maximum, we get

$$J_{max} = \sqrt{\frac{T}{2\theta_r}} - \frac{1}{2} \qquad (10.20)$$

For example, if $\frac{T}{\theta_r} = 100$, $J_{max} = 6$.

The most populous states have the strongest spectral lines, so working close to J_{max} is helpful, for example, in detecting the presence of trace gases such as pollutants in the Earth's atmosphere.

10.7   Comparison of Rotational and Translational Energies

At 0°C, the mean translational energy of an ideal gas molecule is $\frac{3kT}{2} \approx 5.6 \times 10^{-21}$ J.

A molecule of CO has rotational energy from eq. (10.4) of $J(J+1)hcB = J(J+1) \times 3.8 \times 10^{-23}$ J. This means that the rotational energy for $J < 12$ is less than the mean translational energy.

Lecture 11: Rovibrational Energies and Populations

11.1 Harmonic Oscillator

In its simplest form, the vibrational energy of a molecule is described as a harmonic oscillator. We assume that any rotational or electronic effects do not affect the vibrational energy. Because the vibrational frequencies tend to be so much higher than the rotational frequencies, the former assumption seems reasonable. The latter is assumed from the Born-Oppenheimer approximation that notes the mass of electrons is so much smaller than that of the nuclei, that they have negligible effect on the vibrational energy and the wave function can be separated into electronic and rotational-vibrational functions

$$\psi_{int} = \psi_{el}\psi_{rv} \tag{11.1}$$

The original expression in the radial portion of the Schrödinger equation was

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2\mu r^2}{\hbar^2}\left[\varepsilon_{int} - V(r)\right] - J\left(J+1\right)\right]R = 0 \tag{11.2}$$

This is modified to be

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2\mu r^2}{\hbar^2}\left[\varepsilon_{rv} - V(r)\right] - J\left(J+1\right)\right]R = 0 \tag{11.3}$$

by incorporating $\varepsilon_{el}(r) = V(r)$.

Since the rotational energy is given by $\varepsilon_{rot} = \frac{J(J+1)\hbar^2}{2I}$, we can further separate this so that

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2\mu r^2}{\hbar^2}\left[\varepsilon_{vib} - V(r)\right]\right]R = 0 \tag{11.4}$$

A classical oscillator also assumes symmetry between the compression and expansion restoring forces. But as the molecule vibrates with bigger amplitudes this doesn't work, and ultimately it dissociates. As a first step to handling this, the preferred model of the allowed energy levels is known as the Morse potential,

$$V(r) = D_e\left[1 - e^{-\beta(r-r_e)}\right]^2 \tag{11.5}$$

where D_e and β are constants, and r_e is the equilibrium internuclear separation.This agrees with the classical harmonic oscillator when $r \sim r_e$. For the classical harmonic oscillator, the potential is

$$V(r) = \frac{1}{2}k_0\left(r - r_e\right)^2 \tag{11.6}$$

where the force constant k_0 is related to the conventional oscillator frequency by

$$k_0 = \mu(2\pi u)^2 \tag{11.7}$$

Note that as $r \to \infty$, the energy needed for dissociation is given by D_e.

With these assumptions, quantum mechanics gives the vibrational energy as

$$\varepsilon_{vib} = \left(v + \frac{1}{2}\right) h\nu \tag{11.8}$$

with v the vibrational quantum number, and ν is the frequency of oscillation. Converting the latter to wave number units, as ω_e, we have

$$\omega_e = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k_0}{\mu}} \tag{11.9}$$

and

$$G(v) = \frac{\varepsilon_{vib}}{hc} = \left(v + \frac{1}{2}\right)\omega_e \tag{11.10}$$

There is only one state for each vibrational energy level, so

$$g_{vib} \equiv 1 \tag{11.11}$$

11.2   Vibrational Spectroscopy

The selection rule for vibrational transitions is

$$v' - v'' = 1 \tag{11.12}$$

This means that when the vibrational energy level changes, the associated wave number is

$$\tilde{\nu} = \Delta\tilde{\varepsilon}_{vib}$$
$$= \left(v' + \frac{1}{2}\right)\omega_e - \left(v'' + \frac{1}{2}\right)\omega_e$$
$$= \omega_e \tag{11.13}$$

And for pure vibrational spectroscopy there is just a single spectral line. This is because, unlike the rotational spectra. the pure vibrational energy levels are equally spaced. Typically, these lie in the spectral range of 1000-3000 cm^{-1}, or 3-30 μm, in the thermal infrared. Vibrational spectroscopy leads to knowledge about the bond strengths of molecules, via eq. (11.9).

Because the energy associated with vibrational transitions is considerably higher than that due to rotational transitions, when there is a change in v it is associated with changes in J. In fact, we get a series of rotational lines either side of the fundamental vibration wavelength (which disappears). The lower valued wave numbers form what is called the P branch, and the higher valued wave numbers form the R branch.

We also note that, just as for rotational spectroscopy, homonuclear diatomic molecules do not form vibrational lines.

11.3 Rovibrational Spectroscopy: The Simplex Model

Because vibrational transitions also cause rotational transitions, we can consider the additive effects in terms of rovibrational spectra.

$$\tilde{\nu} = \Delta\tilde{\varepsilon}_{rv} = (v' - v'')\omega_e + \left[J'\left(J'+1\right) - J''\left(J''+1\right) \right] B_e \tag{11.14}$$

The selection rules are

$$v' - v'' = 1 \qquad\qquad J' - J'' = \pm 1 \tag{11.15}$$

For the P branch, $J' = J'' - 1$, and for the R branch, $J' = J'' + 1$.

That is,

$$\tilde{\nu}_P = \omega_e - 2B_e J'' \qquad\qquad J'' = 1, 2, 3, ... \tag{11.16}$$

and

$$\tilde{\nu}_R = \omega_e + 2B_e\left(J'' + 1\right) \qquad\qquad J'' = 0, 1, 2, ... \tag{11.17}$$

The spacing of these spectral lines within both branches is again $2B_e$, and we note that the gap at $\tilde{v} = \omega_e$ of $4B_e$ arises naturally from the requirement that there be a change in rotational quantum number.

11.4 Rovibrational Spectroscopy: The Complex Model

While the simplex model gets us started, it is a bit too simple.

The real vibrations are not simple harmonic oscillations, but respond to the Morse potential, indicated by eq. (11.5).

Rotation leads to stretching of the bonds between the atoms comprising the molecule.

Enhanced vibration increases the bond length, changing the moment of inertia.

The net result of all this is to change the selection rules slightly. These become

$$v' - v'' = 1, 2, 3, ... \qquad\qquad J' - J'' = \pm 1 \tag{11.18}$$

For $v'' = 0$, $v' = 1$ is the fundamental transition, $v' = 2$ is the first overtone, $v' = 3$ is the second overtone, etc. The overtone lines are usually much weaker than the fundamental lines.

11.5 The Zero of Energy

From eq. (11.8), when $v = 0$, there is a minimum, non-zero vibrational energy. Whether we choose co to reference the molecular energy to a ground state that includes or excludes the $\frac{\omega_e}{2}$ term is mainly a matter of convention. Here we choose to follow the common spectroscopic practice CO of referencing energies to the lowest vibrational energy, which means we exclude the $\frac{\omega_e}{2}$ term from the partition function.

Lecture 12: Spectral Lines

12.1 Rovibrational Line Notation

To uniquely identify lines in the rovibrational spectrum, the following notation is standard

$$B_{v'}(J'') \qquad \text{where } B = P, R \qquad (12.1)$$

Hence $P_2(5)$ designates a P branch transition from $v' = 2$, $J' = 4$, to $v'' = 1$, $J'' = 5$, or vice versa. $R_1(5)$ designates an R branch transition from $v' = 1$, $J' = 6$, to $v'' = 0$, $J'' = 5$, or vice versa.

12.2 The Vibrational Partition Function

This is given by

$$Z_{vib} = \sum_v g_v e^{-\frac{\varepsilon_{vib}}{kT}} = \sum_{v=0}^{\infty} \exp\left[-\frac{v\theta_v}{T}\right] \qquad (12.2)$$

where the characteristic temperature for vibrational energy was given from eqs. (9.8) and (11.9) as

$$\theta_v = \frac{h\nu}{k} = \frac{hc}{k}\omega_e = \frac{h}{2\pi k}\sqrt{\frac{k_0}{\mu}} \qquad (12.3)$$

and is typically 1000-6000 K.

The vibrational partition function is easier to calculate than its translational or rotational counterparts. Remembering that

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \text{ for } |x| < 1 \qquad (12.4)$$

and noting that if $x = e^{-\frac{\theta_v}{T}}$, eq. (12.2) becomes

$$Z_{vib} = \sum_{v=0}^{\infty} x^v = \frac{1}{1-x} = \frac{1}{1-e^{-\frac{\theta_v}{T}}} \qquad (12.5)$$

Differentiating $\ln Z_{vib}$ to get the terms we need for thermodynamics, we have

$$T\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{\frac{\theta_v}{T}}{e^{\frac{\theta_v}{T}} - 1} \qquad (12.6)$$

and

$$\left[\frac{\partial}{\partial T}T^2\left(\frac{\partial \ln Z_{vib}}{\partial T}\right)\right]_V = \frac{\left(\frac{\theta_v}{T}\right)^2 e^{\frac{\theta_v}{T}}}{\left(e^{\frac{\theta_v}{T}} - 1\right)^2} \qquad (12.7)$$

From which the vibrational contributions to the internal energy, entropy, specific heat, etc. can be calculated, as before.

While we can show the expected results that

$$\lim_{T \to \infty} \left(\frac{u}{R^*T} \right)_{vib} = 1 \tag{12.8}$$

and

$$\lim_{T \to \infty} \left(\frac{c_v}{R^*} \right)_{vib} = 1 \tag{12.9}$$

this requires $T \gg \theta_v$. So the classical equipartition of vibrational energy contributions does not make a full contribution from statistical thermodynamics until very high temperatures.

At room temperatures, for example, if $\frac{T}{\theta_v} \sim 3$, we have $\frac{u}{R^*T} \sim 0.1$ and $\frac{c_v}{R^*} \sim 0.5$.

12.3 Extension to Polyatomic Vibrations

A molecule with n atoms can have multiple vibrational modes. The number will depend on whether it is a linear or nonlinear molecule. (n atoms $\to 3n$ degrees of freedom)

Linear molecules have $3n - 5$ vibrational degrees of freedom, involving symmetric and asymmetric stretching, and bending with two degrees of freedom. (translation=3, rotation=2, vibration=$3n - 5$)

Nonlinear molecules have $3n - 6$ vibrational degrees of freedom, losing one bending degree of freedom compared with linear molecules. (translation=3, rotation=3, vibration=$3n - 6$)

Each separate vibrational mode has its characteristic frequency and characteristic vibrational temperature. The total vibrational partition function is the product of all the possibilities.

$$Z_{vib} = \prod_{i=1}^{m} \frac{1}{1 - e^{-\frac{\theta_{vi}}{T}}} \tag{12.10}$$

where $m = 3n - 5$ for linear molecules, and $m = 3n - 6$ for nonlinear molecules.

The symmetry factors for polyatomic molecules can get complicated. For example, H_2O, which has an asymmetric top structure, has $\sigma = 2$, whereas CH_4 has a spherical top structure with $\sigma = 12$. The rotational degeneracies also appear to change from the $(2J + 1)$ of diatomic molecules.

12.4 General Comments Regarding Electronic Energies

While the electron levels of a hydrogen atom are well studied, and reasonably understandable, the complications that arise in higher atomic number atoms, and in molecules make this a complex field of study. We note here that because the characteristic temperature for the electronic partition function is very high (on order 10^5 K) for many problems the vast majority of molecules remain in their electronic ground state, or at least very few electronic states need to be considered.

A shift to an electronic energy state above the ground state affects the vibrational and rotational energies in the higher state. The force constant becomes less, the inter-nuclear spacing greater, the moment inertia increases, and so on. All of this creates measurable effects on the associated spectroscopy.

Nevertheless, for visible and ultraviolet portions of the spectrum, electronic transitions become the dominant source of absorption and emission spectra.

Lecture 13: Radiative Transitions

13.1 Line Shapes

There is a temptation to treat spectral lines as being infinitesimally thin, as we have already talked about discrete frequencies of transition. However, even if there weren't other factors that change this, the uncertainty principle would provide a minimum thickness to any spectral line. So in general we refer to two separate components of any spectral line: its line strength S, and its line profile, $P(\nu - \nu_0)$. We relate these by defining a spectral emission coefficient $\kappa(\nu)$, which expresses the energy radiated per unit time, per unit frequency interval, per unit mass of gas, per unit solid angle.

$$\kappa(\nu) = SP(\nu - \nu_0) \tag{13.1}$$

The line profile is normalized such that

$$\int_{-\infty}^{\infty} P(\nu - \nu_0)d\nu = 1 \tag{13.2}$$

This means that the line strength is a measure of the total emission by the line

$$S = \int_{-\infty}^{\infty} \kappa(\nu)d\nu \tag{13.3}$$

By Kirchhoff's law, which requires the absorption and emission coefficients to be equal at the same frequency, the absorption line profile must be the same as the emission line profile for the same conditions.

Our main interest here will be in relating line strengths to the earlier material on statistical populations, but before doing so we can briefly examine the line profiles.

13.2 Line Profiles

These are characterized mainly by their half-width α, which is usually taken to be the distance from the centre that the profile has dropped to half its maximum. The half-width may appear as a frequency, wave number or wavelength, depending on the context. Note that Laurendeau use full width at half maximum for his line widths FWHM=2α.

For example, the natural profile can be written

$$P(\nu - \nu_0) = \frac{2\alpha_n}{4\pi^2 \left[(\nu - \nu_0)^2 + \left(\frac{\alpha_n}{2}\right)^2\right]} \tag{13.4}$$

where the natural width may be less than 10^{-5} nm, expressed as a wavelength. The shape of this type of profile is called a Lorentz profile.

For gases under many conditions, the motion of the gas itself causes a broadening of the line profile through the Doppler effect. This may also be referred to as temperature broadening, because the velocities depend on temperature.

The Doppler shift in frequency, due to velocity v_x of either the source of the receiver is

$$\nu' = \nu_0 \left(1 + \frac{v_x}{c} \right) \tag{13.5}$$

So that

$$v_x = \frac{c \left(\nu' - \nu_0 \right)}{\nu_0} \tag{13.6}$$

To each velocity between v_x and $v_x + dv_x$ there is a corresponding frequency between ν' and $v' + d\nu'$, such that

$$dv_x = \frac{c}{\nu_0} d\nu' \tag{13.7}$$

From the Maxwell distribution of velocities, we had

$$dN = N \left(\frac{m}{2\pi kT} \right)^{1/2} \exp \left(-\frac{m}{2kT} v_x^2 \right) dv_x \tag{13.8}$$

Now the coefficient $\kappa(\nu)$ at ν' must be proportional to the partial population in dv_x, so from the previous three equations we have

$$\kappa(\nu') = S \frac{c}{\nu_0} \left(\frac{m}{2\pi kT} \right)^{1/2} \exp \left[-\frac{mc^2}{2kT\nu_0^2} \left(\nu' - \nu_0 \right)^2 \right] d\nu' \tag{13.9}$$

From which the half-width of the Doppler broadened line is obtained as

$$\alpha_D = \frac{\nu_0}{c} \left(\frac{2kT}{m} \ln 2 \right)^{1/2} \tag{13.10}$$

For example, for CO at 300 K, $\alpha_D \sim 5.5 \times 10^{-3}$ nm, considerably higher than the natural half-width.

The other common reason for the line to broaden is due to collisions with other molecules, termed collision or pressure broadening. These interrupt the natural lifetime of the transition. The resulting profile is also Lorentzian, but with a half-width of

$$\alpha_L = \frac{1}{4\pi\tau_{coll}} = \alpha_{L,0} \frac{p}{p_0} \left(\frac{T_0}{T} \right)^{1/2} \tag{13.11}$$

where τ_{coll} is the mean time between collisions, that depends on temperature and pressure, and the subscript 0 refers to any reference condition. That is, the half-width increases

proportional to pressure, and decreases proportional to $\sqrt{T}$. At STP the collision half-width is almost an order of magnitude larger than the Doppler half width. For high pressures, pressure broadening has a major effect on radiative transfer, as many gaps between spectral lines get filled. For example, the lower atmosphere of Venus, at about 100 bar of CO_2, is greatly affected by pressure broadening. e.g. the half-width for CO_2 on Venus$\approx 100(\frac{300}{700})^{1/2} \approx 65$ times that at the Earth's surface.

The above theory is somewhat approximate, however, as the collisional effect can be more complicated, and the profile also departs from a Lorentzian as it gets further from its centre. This causes some controversy in the Earth's atmosphere, where absorption of thermal radiation in the 8-13 μm window is greatly affected by high humidity (the absorption coefficient rises as e^2, where e is the water vapour pressure) despite no obvious spectral lines. One explanation is that the far wing profiles of the many water vapour rotation lines are sufficiently non-Lorentzian far from the line centres that their cumulative effect appears like continuous absorption. Here, the term continuous absorption describes absorption of radiation in the absence of spectral detail. It is generally unusual for gases, but common for liquids and solids.

13.3   Line Strengths

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The strength of a spectral line depends on the population of the initial state, as well as the probabilities of transitions into or out of the initial state. These probabilities are related to the Einstein coefficients as follows.

1. Probability of spontaneous emission, A_{ul}, per unit time, from an upper state u to a lower state l. This emission is in a random direction.

2. Probability of stimulated emission, B_{ul}, per unit time, per unit radiant energy density in the space surrounding the emitter, per unit frequency interval. This emission is with the same frequency and phase, and in the same direction, as the incident photon.

3. Probability of absorption, B_{lu}, per unit time, per unit radiant energy density in the space surrounding the emitter, per unit frequency interval.

Note that because we are dealing with photon absorption and emission, and photons are bosons, we have no worries about filling up any of the energy states to saturation.

Let us consider radiative transitions between two arbitrary levels, u and l, upper and lower, respectively, with population densities n_u and n_l.

The rate of population transfer into or out of each level is given by

$$\frac{dn_l}{dt} = n_u A_{ul} - n_l B_{lu}\rho_\nu + n_u B_{ul}\rho_\nu + Q_{ul}n_u \qquad (13.12)$$

and

$$\frac{dn_u}{dt} = -n_u A_{ul} + n_l B_{lu}\rho_\nu - n_u B_{ul}\rho_\nu - Q_{ul}n_u \qquad (13.13)$$

where ρ_ν is the density of radiant energy at frequency ν, with units of Jm^{-3}, and Q is the rate of quenching in units of s^{-1}.

There is a little confusion in the various texts regarding the definition of ρ_ν, as being either density at ν, or density per frequency interval (which seems better). Either way the product $B\rho_\nu$ must be in units of s^{-1}. The quenching is included in the general case to account for non-radiative transitions that occur due to collisions with other molecules. The quenching increases with pressure, and is much higher for asymmetric molecules than for atoms, given the ease of changing rotational and vibrational energy modes. However, we can apply a low pressure limit ($Q_{ul} \approx 0$), and invoke radiative equilibrium to examine the coefficients because these are constants for particular atoms or molecules.

Consider radiative transitions only, and note that the change in occupation number is associated with a change in radiant energy, with $h\nu Y(\nu)$ per photon per Hz. Here $Y(\nu)$ is the line profile [$Y(\nu) = P(\nu - \nu_0)$ in eq. (13.1)]. We have the local spectral power density p_ν ($\text{W m}^{-3}\text{ Hz}^{-1}$) as

$$p_\nu = h\nu \left(\frac{dn_l}{dt}\right) Y(\nu) = h\nu A_{ul} n_u Y(\nu) + h\nu \left[B_{ul} n_u - B_{lu} n_l\right] \rho_\nu Y(\nu) \qquad (13.14)$$

Now the density of radiant energy is directly proportional to the spectral radiance ($\text{W m}^{-2}\text{ sr}^{-1}\text{ Hz}^{-1}$)

$$I_\nu = \frac{\rho_\nu c}{4\pi} \qquad (13.15)$$

Note that Laurendeau uses I for irradiance, and J for radiance (which is not usual). The change in spectral radiance with optical path can be written

$$dI_\nu = \frac{p_\nu}{4\pi} ds \qquad (13.16)$$

So that eqs. (13.14), (13.15) and (13.16) give

$$\frac{dI_\nu}{ds} = \left(\frac{h\nu}{4\pi}\right) A_{ul} n_u Y(\nu) + \frac{h\nu}{c} \left[B_{ul} n_u - B_{ln} n_l\right] I_\nu Y(\nu) \qquad (13.17)$$

In radiative equilibrium, the sum of the rates for spontaneous and induced emission must equal the rate for absorption, and $\frac{dI_\nu}{ds} = 0$, or $p_\nu = 0$, and eq. (13.14) gives

$$n_l B_{lu} \rho_\nu = n_u \left[B_{ul} \rho_\nu + A_{ul}\right] \qquad (13.18)$$

Referring back to the Maxwell-Boltzmann distribution for the ratio of populations of two states in equilibrium (eq. 6.20), we had earlier

$$\frac{n_j g_k}{n_k g_j} = \exp\left(-\frac{\varepsilon_j - \varepsilon_k}{kT}\right) \qquad (13.19)$$

which we rewrite in terms of u and l as

$$\frac{n_u}{n_l} = \frac{g_u}{g_l} \exp\left(-\frac{\varepsilon_u - \varepsilon_l}{kT}\right) = \frac{g_u}{g_l} e^{-\frac{h\nu}{kT}} \qquad (13.20)$$

because $\varepsilon_u - \varepsilon_l = h\nu$.

Solving eq. (13.18) and eq. (13.20) for ρ_ν, we find

$$\rho_\nu = \frac{\frac{A_{ul}}{B_{ul}}}{\left(\frac{g_l B_{lu}}{g_u B_{ul}}\right) \exp\left(\frac{h\nu}{kT}\right) - 1} \tag{13.21}$$

Note that this result comes from a classical MB distribution.

Anticipating the result for the spectral energy density for a blackbody in radiative equilibrium, i.e. the Planck distribution, we also have

$$\rho_\nu^B = \frac{8\pi h\nu^3}{c^3} \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1} \tag{13.22}$$

Comparing eq. (13.21) and eq. (13.22), we have agreement if

$$\frac{B_{lu}}{B_{ul}} = \frac{g_u}{g_l} \tag{13.23}$$

and

$$A_{ul} = \frac{8\pi h\nu^3}{c^3} B_{ul} \tag{13.24}$$

Eq. (13.23) indicates that induced absorption coefficient $\approx$ induced emission coefficient, if the degeneracies are similar. But because there tends to be a greater population in the lower level, the incident photon is more likely to induce absorption than emission, so that induced absorptive transitions dominate. The balance that maintains radiative equilibrium is made up by the spontaneous emission term (A_{ul}).

Even though they have been derived under conditions of radiative equilibrium, the Einstein coefficients are fundamental microscopic parameters and retain their values in non-equilibrium conditions. Once one is known, the others follow directly from the above equations, and normally only A_{ul} is quoted for a given molecule and energy transition. Finding the value of A_{ul} requires delving back into the theory of dipole moments and quantum states, from which

$$A_{ul} = \frac{16\pi^3 \nu^3}{3\varepsilon_0 h c^3} M_{ul}^2 \tag{13.25}$$

where M_{ul} is the transition dipole moment of the atom or molecule in its upper state. So there has to be a dipole moment to get a transition. Also note that the transitions are stronger at higher frequency, for similar dipole moments. Hence the strongest spectral lines tend to be at the shortest wavelengths.

Lecture 14: Blackbody Radiation

14.1 Example: Absorption Spectroscopy

Laurendeau 11.3

For simplicity, consider an atomic case, where the upper and lower levels signify the first excited and ground electronic states, so that $\frac{n_u}{n_l} \ll 1$ at thermodynamic equilibrium. For a weak light source, eq. (13.17) becomes

$$\frac{dI_\nu}{ds} = -k_\nu I_\nu \tag{14.1}$$

where the spectral absorption coefficient (also called the volume absorption coefficient), k_ν is given by

$$k_\nu = \left(\frac{h\nu}{c}\right) B_{lu} n_l Y(\nu) \tag{14.2}$$

Assuming k_ν is constant along a pathlength L gives the familiar Bouguer law

$$I_\nu(L) = I_\nu(0)e^{-k\nu L} \tag{14.3}$$

Experimentally we can measure the integrated absorption, W_{lu}, defined as

$$W_{lu} = \int \left[1 - \frac{I_\nu(L)}{I_\nu(0)}\right] d\nu = \int \left[1 - e^{-k_\nu L}\right] d\nu \tag{14.4}$$

By keeping the absorption weak, the total strength of the line can be found as K_{lu}

$$W_{lu} = \int k_\nu L d\nu = K_{lu} L \tag{14.5}$$

From eq. (14.2) we also have

$$K_{lu} = \int k_\nu d\nu = \left(\frac{h\nu_{ul}}{c}\right) B_{lu} n_l \tag{14.6}$$

So that the concentration of atoms in the ground state is given by

$$n_l = \frac{cW_{lu}}{h\nu_{ul} B_{lu} L} \tag{14.7}$$

The total concentration of the absorbing gas is then found from the partition function for this mode

$$n = \frac{n_l}{g_l} \exp\left(\frac{\varepsilon_l}{kT}\right) \tag{14.8}$$

If a second measurement is then made for n_k, involving a different energy level, the temperature can also be found.

14.2 Summary of Line Strength: Equivalent Width and the Curve of Growth

From the previous section, the line strength for absorption depends on the population of the lower level, n_l, and increases with frequency. W is termed the equivalent width of the line, being also the width of a rectangular totally absorbing line. W depends on the absorber concentration. In other words, for low absorber amounts we have a linear dependence on absorption, given by eq. (14.5). For larger absorber amounts, the dependence is non-linear: once radiation at the central frequency has all been absorbed, additional absorption occurs in the wings of the line only, and the total absorption increases more and more slowly. The overall dependence of W on absorber amount is termed the curve of growth. For example, the average absorption over some finite spectral interval $\Delta\nu$ in the weak-line limit, where S is the line strength and u is the mass of absorber per unit cross section of path, is

$$\bar{A} = \frac{Su}{\Delta\nu} \tag{14.9}$$

The counterpart of the strong-line limit, for a Lorentz line shape is

$$\bar{A} = \frac{2}{\Delta\nu} \left(S\alpha_L u\right)^{1/2} \tag{14.10}$$

Remembering from eq. (13.11) the pressure and temperature dependence of the line width, the strong-line absorption varies as $p^{1/2}T^{-1/4}$. For Doppler broadened lines, the weak limit remains the same, but the strong limit grows only as $(\ln u)^{1/2}$.

14.3 Bose-Einstein Statistics for the Photon Gas

Now we return to equilibrium radiation, and the background behind eq. (13.11). Noting that photons are bosons, their distribution is governed by Bose-Einstein statistics, which we noted earlier can be written:

$$N_j = \frac{g_j}{\exp\left[\frac{\varepsilon_j - \mu}{kT}\right] - 1} \tag{14.11}$$

Photons can be absorbed and emitted a number of different ways. While the total energy must be conserved, there is no such constraint on the number of photons. Consequently we can relax the criterion we had earlier that $\sum N_j = $ constant. The chemical potential in eq. (14.11) must therefore vanish.

$$N_j = \frac{g_j}{\exp\left[\frac{\varepsilon_j}{kT}\right] - 1} \tag{14.12}$$

Noting that we can have any number of photons, and that the energy of each photon can be expressed as $\varepsilon = h\nu$, we can turn eq. (14.12) into a continuous distribution, where $N(\nu)d\nu$ is the number of photons, and $g(\nu)d\nu$ is the number of photon states in the frequency range ν to $\nu + d\nu$.

$$N(\nu)d\nu = \frac{g(\nu)d\nu}{\exp\left[\frac{h\nu}{kT}\right] - 1} \tag{14.13}$$

14.4   Photon Quantum States

All we have for photons is their kinetic energy of translation. They have no spin, no vibrations, and no electronic levels of their own. They do have polarization, however, giving two independent states because of that.

The number of quantum states due to translational energy is found similarly to particle translational energy. The number of translational states for all frequencies less than ν is the octant of the sphere of radius n, where n is the total quantum number. That is,

$$M_\nu = \frac{1}{8}\frac{4\pi n^3}{3} = \frac{\pi n^3}{6} \tag{14.14}$$

To find the number of states in the frequency range ν to $\nu + d\nu$, we differentiate eq. (14.14), obtaining

$$g(\nu)d\nu = 2dM_\nu = \pi n^2 dn \tag{14.15}$$

where the factor of 2 accounts for the two polarization states. Eq. (14.13) thus becomes

$$N(\nu)d\nu = \frac{\pi n^2 dn}{\exp\left[\frac{h\nu}{kT}\right] - 1} \tag{14.16}$$

14.4.1   Standing Waves

To relate the total quantum number to the frequency, we can consider the equilibrium occurring in a cubic cavity of dimension L. The photons confined to this blackbody cavity set up standing waves, which can be thought of as the superposition of two travelling waves reflected by the cavity walls, for each of the three dimensions. These occur for quantized values of the electromagnetic wave at a given frequency.

For example, in the $+x$ direction, an electromagnetic wave of the form

$$E_{+x} = E_0 \sin\left(\frac{2\pi x}{\lambda} - \omega t\right) = E_0 \sin\left(k_x x - \omega t\right) \tag{14.17}$$

where the wave number in the x direction can be related to the spacial frequency ν_x as

$$k_x = \frac{2\pi \nu_x}{c} \tag{14.18}$$

Combining this with a wave of equal magnitude travelling in the opposite direction gives the standing wave

$$\begin{aligned}
E_s &= E_{+x} + E_{-x} \\
&= E_0 \left[\sin\left(k_x x - \omega t\right) + \sin\left(k_x x + \omega t\right)\right] \\
&= 2E_0 \sin\left(k_x x\right) \cos\left(\omega t\right)
\end{aligned} \tag{14.19}$$

The boundary conditions require $E_s = 0$ at $x = 0$, $x = L$, so that

$$k_x L = n_x \pi \qquad \text{for } n_x = 1, 2, 3, ... \tag{14.20}$$

For the full 3D situation we obtain

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \left(\frac{\pi}{L}\right)^2 \left(n_x^2 + n_y^2 + n_z^2\right) \tag{14.21}$$

Putting this together with eq. (14.18), we have

$$k^2 = \frac{4\pi^2\nu^2}{c^2} = \frac{\pi^2 n^2}{L^2} \tag{14.22}$$

Thus

$$n = \frac{2L\nu}{c} \tag{14.23}$$

and more generally

$$n^3 = \frac{8V\nu^3}{c^3} \tag{14.24}$$

Finally, we differentiate eq. (14.24) to obtain

$$n^2 dn = \frac{8V}{c^3}\nu^2 d\nu \tag{14.25}$$

which is what we need for eq. (14.16).

14.4.2 Photon Degeneracy Within a Cavity

The number of states is proportional to the volume of the cavity, and to the square of the frequency

$$g(\nu) = \frac{8\pi V}{c^3}\nu^2 \tag{14.26}$$

14.5 Planck Distribution Law for Equilibrium Radiation

Each photon has energy $h\nu$, so that the energy density is

$$\rho_\nu d\nu = \frac{h\nu N(\nu) d\nu}{V} \tag{14.27}$$

and the density itself, from eq. (14.13) and eq. (14.26) is

$$\rho_\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{\exp\left[\frac{h\nu}{kT}\right] - 1} \tag{14.28}$$

which is what we already assumed for the Planck distribution in eq. (13.11).

The radiant energy density ($\mathrm{J\ m^{-3}}$) is related to the spectral radiance ($\mathrm{W\ m^{-2}\ sr^{-1}}$) from eq. (13.4), and this is isotropic. Writing this conventionally as B_ν, we have the Planck function.

$$B_\nu = \frac{\rho_\nu c}{2\pi} = \frac{2h}{c^2} \frac{\nu^3}{\exp\left[\frac{h\nu}{kT}\right] - 1} \tag{14.29}$$

The blackbody flux density ($\mathrm{W\ m^{-2}\ Hz^{-1}}$) across a surface (irradiance, or sometime emissive power density) is

$$F_\nu = \pi B_\nu = \frac{2\pi h}{c^2} \frac{\nu^3}{\exp\left[\frac{h\nu}{kT}\right] - 1} \tag{14.30}$$

We can integrate this over all frequencies as follows.

Setting

$$x = \frac{h\nu}{kT} \tag{14.31}$$

$$F = \int F_\nu d\nu = \frac{2\pi h}{c^2} \int_0^\infty \frac{\frac{d\nu^4}{4}}{e^x - 1} = \frac{2\pi h^{-3}k^4T^4}{c^2} \int_0^\infty \frac{x^3 dx}{e^x - 1} \tag{14.32}$$

From tables of integrals we usually just look up the answer for such integrals, finding

$$\int_0^\infty \frac{x^3}{e^x - 1}dx = \frac{\pi^4}{15} \tag{14.33}$$

Hence we have the Stefan-Boltzmann law

$$F = \sigma T^4 \tag{14.34}$$

where

$$\sigma = \frac{2\pi^5 k^4}{15h^3c^2} = 5.67 \times 10^{-8}\ \mathrm{W\ m^{-2}\ K^{-4}} \tag{14.35}$$

is the Stefan-Boltzmann constant. From classical thermodynamics (as we showed in PHYS 231), you can independently show that $F \propto T^4$, but the constant of proportionality requires integration over the Planck function.

Lecture 15: Electron Gases

15.1 Approximations to the Planck Function for Different Wavelength Extremes

We can switch from B_ν to B_λ, noting that $\frac{d\nu}{d\lambda} = -\frac{\nu}{\lambda}$, obtaining

$$B_\lambda = B_\nu \left| \frac{d\nu}{d\lambda} \right| = \frac{2hc^2}{\lambda^5} \frac{1}{\exp\left[\frac{hc}{\lambda kT} \right] - 1} \tag{15.1}$$

For long wavelengths, $hc, \ll \lambda kT$, we have

$$B_{\lambda,RJ} \approx \frac{2hc^2}{\lambda^5} \frac{1}{1 + \frac{hc}{\lambda kT} - 1} = \frac{2ckT}{\lambda^4} \tag{15.2}$$

which is the Rayleigh-Jeans law, and known long before the Planck distribution. Similarly, for short wavelengths, $hc \gg \lambda kT$, and

$$B_{\lambda,Wien} \approx \frac{2hc^2}{\lambda^5} \exp\left[-\frac{hc}{\lambda kT} \right] \tag{15.3}$$

which is Wien's law (not to be confused with Wien's displacement law).

Setting

$$x = \frac{hc}{\lambda kT} \tag{15.4}$$

we find that

$$B_{\lambda,Wien} \propto x^5 e^{-x} \tag{15.5}$$

On differentiating, this has a maximum at $x = 5$, from which we have that the maximum emission occurs at a wavelength that is inversely proportional to T, expressed as Wien's displacement law

$$\lambda_{max} \approx \frac{hc}{5kT} \tag{15.6}$$

The precise solution must be found numerically, and differs by 0.3%.

15.1.1 Applications in Using the Planck Function

Brightness temperature: by directly measuring the radiance, $I_\lambda = B_\lambda(T)$, emitted from an object at some distance, assuming no changes in radiance during transit, the brightness temperature of the object is inferred as

$$T_b = B_\lambda^{-1}(I_\lambda) \tag{15.7}$$

Common examples are in medicine (non intrusive patient temperature), furnaces (where a thermometer would melt), and astronomy to estimate stellar temperatures. One issue with this is that the brightness temperature will be less than the physical temperature if

the emissivity of the object is less than 1, and the emissivity may be unknown.

Colour temperature: by making radiance measurements at two wavelengths, and taking their ratio, the effect of emissivity can be removed (provided it does not change between the two wavelengths.) Thus, if $I_{\lambda_{1,2}} = \varepsilon B_{\lambda_{1,2}}(T)$, then T is obtained from

$$\frac{I_{\lambda_1}}{I_{\lambda_2}} = \frac{\lambda_2^5}{\lambda_1^5} \frac{\exp\left[\frac{hc}{\lambda_2 kT}\right] - 1}{\exp\left[\frac{hc}{\lambda_1 kT}\right] - 1} \tag{15.8}$$

If Wien's law can be applied by using short wavelengths, this reduces to give

$$T = \frac{hc}{k} \frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2} \frac{1}{\ln\left(\frac{I_{\lambda_1}}{I_{\lambda_2}} \frac{\lambda_1^5}{\lambda_2^5}\right)} \tag{15.9}$$

again with applications to astronomy, flames, etc.

Note that at long wavelengths, the ratio technique fails completely, as can be verified from the Rayleigh-Jeans approximation.

15.2 Internal Energy and Entropy of Blackbody Radiation

The internal energy per unit volume is given directly from the energy density as

$$\frac{U}{V} = \int \rho_\nu d\nu = \frac{8\pi^5}{15} \frac{(kT)^4}{(hc)^3} \tag{15.10}$$

For entropy, going back to lecture 7, we had

$$S = \frac{U}{T} - k \sum_i g_i \ln\left(1 - \exp\left[-\frac{\varepsilon_i}{kT}\right]\right) \tag{15.11}$$

where the chemical potential is set to zero for photons. Using eq. (15.10), and treating the energies as a continuous distribution, we have

$$S = \frac{U}{T} - 8\pi kV \left(\frac{kT}{hc}\right)^3 \int_0^\infty x^2 \ln\left(1 - e^{-x}\right) dx \tag{15.12}$$

Using eq. (15.10) and integrating by parts gives

$$S = \frac{8\pi^5 kV}{15} \left(\frac{kT}{hc}\right)^3 + \frac{8\pi kV}{3} \left(\frac{kT}{hc}\right)^3 \int \frac{x^3}{e^x - 1} dx = 8\pi^5 kV \left(\frac{kT}{hc}\right)^3 \left(\frac{1}{15} + \frac{1}{45}\right) \tag{15.13}$$

So that

$$S = \frac{32}{45} \pi^5 kV \left(\frac{kT}{hc}\right)^3 \tag{15.14}$$

15.3 Statistical Thermodynamics of the Crystalline Solid

Laurendeau 13 The lattice structure of metallic crystals implies N metallic ions are equivalent to $3N$ linear harmonic oscillators that would have specific heat of $3R$, which is what is observed at room temperature.

At lower temperatures, this model fails, and what is observed instead is

$$\lim_{T \to 0} \frac{c_v}{R} \propto T^3 \tag{15.15}$$

Because the oscillators are distinguishable, they follow uncorrected, rather than corrected Maxwell-Boltzmann statistics. For these, the number of microstates for a given macrostate is

$$W_{MB} = N! \prod_j \frac{g_j^{N_j}}{N_j!} \tag{15.16}$$

that we showed in lecture 5.

This yields the equilibrium particle distribution

$$\frac{N_j}{N} = \frac{g_j e^{-\frac{\varepsilon_j}{kT}}}{Z} \tag{15.17}$$

where

$$Z = \sum_j g_j e^{-\frac{\varepsilon_j}{kT}} \tag{15.18}$$

The internal energy and specific heat follow, as before,

$$U = NkT^2 \left[\frac{\partial \ln Z}{\partial T} \right]_V \tag{15.19}$$

$$C_V = Nk \left[\frac{\partial}{\partial T} T^2 \left(\frac{\partial \ln Z}{\partial T} \right) \right]_V \tag{15.20}$$

The entropy can be derived from eq. (15.16), using Stirling's approximation,

$$S = k \ln W_{MB} = kN \ln N - kN + k \sum_j \left[N_j \ln g_j - N_j \ln N_j + N_j \right] \tag{15.21}$$

From eq. (15.17),

$$S = kN \ln N + k \sum_j N_j \left[\ln \left(\frac{Z}{N} \right) + \frac{\varepsilon_j}{kT} \right] \tag{15.22}$$

From eq. (15.19),

$$S = Nk \ln Z + \frac{U}{T} = Nk \left(T \left[\frac{\partial \ln Z}{\partial T} \right]_V + \ln Z \right) \tag{15.23}$$

which differs from the expression for entropy when the particles are indistinguishable

$$S = Nk \left(T \left[\frac{\partial \ln T}{\partial T} \right]_V + \ln \left(\frac{Z}{N} \right) + 1 \right) \tag{15.24}$$

To explain the behaviour of heat capacity at low temperature, Einstein proposed that the oscillators were non-interacting, each with

$$Z_{vib} = \left(1 - e^{-\theta_E/T} \right)^{-1} \tag{15.25}$$

where $\theta_E = \frac{h\nu_E}{k}$ is the Einstein temperature.

From eq. (15.25) and eq. (15.20), noting there are $3N$ oscillators, we find

$$\frac{c_V}{R} = \frac{3 \left(\frac{\theta_E}{T} \right)^2 e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1 \right)^2} \tag{15.26}$$

So that

$$\lim_{\theta_E/T \to \infty} \frac{c_V}{R} = \frac{3 \left(\frac{\theta_E}{T} \right)^2 e^{\theta_E/T}}{e^{2\theta_E/T}} = 3 \left(\frac{\theta_E}{T} \right)^2 e^{-\theta_E/T} \tag{15.27}$$

which is not what is observed. The other limit, as T increases tends to 3, which is ok. This led to the Debye theory of crystalline solids, which recognizes that the oscillators become coupled at low oscillating frequency, but decoupled at high enough frequency (the Debye frequency.) As T tends to 0, the frequency distribution favours lower frequencies, so more coupling occurs, and the heat capacity is shared amongst more and more oscillators. This theory ultimately gives the observed T^3 dependency.

Debye theory also allows the entropy to be determined at low temperatures, where it is found that

$$\lim_{\theta_D/T \to \infty} \frac{s}{R} = \frac{4\pi^4}{5} \left(\frac{T}{\theta_D} \right)^3 \tag{15.28}$$

where $\theta_D = \frac{h\nu_D}{k}$ is the Debye temperature, and ν_D is the Debye frequency, where the oscillators are uncoupled. Values of the Debye temperature vary among elements, from 86K for lead to 980K for Beryllium.

Lecture 16: More Electrons, Entropy and 2$^{\text{nd}}$ Law

16.1 Electrons in Solids

16.1.1 The Fermi Energy

We know that electrons are fermions. There can be at most one electron per energy state. So can we use corrected Maxwell-Boltzmann statistics in the dilute limit for electrons, or must we use Fermi-Dirac?

If we consider the electrons to act like an ideal gas, for example, then we could use the translational partition function developed earlier.

$$Z = \left(\frac{2\pi m k T}{h^2} \right)^{1/2} V \tag{16.1}$$

and we want $\frac{Z}{N} \gg 1$ for the dilute limit to apply. Putting in the mass of an electron (9.1×10^{-31} kg), we have

$$Z = 2.3 \times 10^{21} T^{\frac{3}{2}} V$$

If we assume that only one electron is free per atom, we still get $O(10^{23})$ electrons per cm^3. This means that $\frac{Z}{N} \ll 1$ for electrons, and we can't use the dilute limit. Thus

$$n_j = \frac{g_j}{\exp\left[\frac{\varepsilon_j - \mu}{kT} \right] + 1} \tag{16.2}$$

As $T \to 0$, we have therefore only two possibilities for the number of electrons per energy state:

$$\left(\varepsilon_j - \mu_0 \right) > 0 \qquad \frac{n_j}{g_j} = 0 \tag{16.3}$$

or

$$\left(\varepsilon_j - \mu_0 \right) < 0 \qquad \frac{n_j}{g_j} = 1 \tag{16.4}$$

where μ_0 is the chemical potential at absolute zero.

Without knowing very much about electrons in solids we can already infer that there must be some critical energy,

$$\varepsilon_F = \mu_0 \tag{16.5}$$

that exists near absolute zero that separates totally-filled from completely-empty electronic states. The exclusion principle means that we have to put the electrons somewhere. Therefore there will be a maximum energy, even at absolute zero, that is needed to accommodate these electrons. We call ε_F the Fermi energy.

Again going back to earlier material, we had the number of microstates for a Fermi-Dirac system as

$$W_{FD} = \prod_j \frac{g_j!}{n_j! \, (g_j - n_j)!} \tag{16.6}$$

So, for $\varepsilon < \varepsilon_F$, $n_j = g_j$, and $W_{FD} = 1$.

Conversely, for $\varepsilon > \varepsilon_F$, $n_j = 0$, and again $W_{FD} = 1$.

Either way, the entropy $S = k \ln W = 0$ at absolute zero for Fermi-Dirac statistics. The system is perfectly ordered, with either zero or complete occupancy.

16.1.2 Band Structures

When we consider the atoms in a solid, they have energy levels as vibrators. If the solid is crystalline, these occur in regularly spaced positions that are tractable to analysis. Amorphous solids are also interesting, but left for another time. The ions in a metallic crystal have electronic energies that overlap as the spacing between the atoms decreases (e.g. with lower T) forming energy bands. Each energy band is made up of a large number of individual energy levels from the neighbouring ions. An energy band is characterized by its discrete spacing from other bands caused by the existence of forbidden regions that cannot be accessed. In general, there usually emerge two particular bands:

- The valence band, which is the most populated band.

- The conduction band, which is the band with the next highest energy above the valence band.

- Between the valence band and the conduction band there is a discrete energy gap.

If the energy within the band is less than the Fermi energy, it is populated. Otherwise, it is empty.

For an insulator, there is a large gap between the Fermi energy within the valence band and the conduction band, which is therefore empty. At ordinary temperatures, there are no free electrons to provide conduction.

For metals, however, the Fermi energy lies in the conduction band, allowing the existence of free electrons, even at room temperature. The free movement of these electrons, unperturbed by the positive ions in the crystal lattice, allows them to be treated as an ideal gas.

Semiconductors form a special (but oh so important) case that is intermediate between insulators and metals. They are studied in their own right.

16.2 Thermodynamic Properties of an Electron Gas

These have translational energy that creates a somewhat similar set of quantum states as we have already studied. The added complication with electrons is that they have spin.

Analogous to the polarization of photons, this gives twice as many possible states. Adapting our earlier work (eq. 8.4) by adding a factor of 2, we have

$$D(\varepsilon)d\varepsilon = 4\pi \left[\frac{2m_e}{h^2}\right]^{3/2} V\varepsilon^{1/2}d\varepsilon \tag{16.7}$$

This is also the number of electrons with translational energies between ε and $d\varepsilon$ at absolute zero. Therefore, from eq. (16.2), the number at any temperature is given by

$$n(\varepsilon) = \frac{D(\varepsilon)}{\exp\left[\frac{\varepsilon-\mu}{kT}\right] + 1} \tag{16.8}$$

and the total number of electrons becomes

$$N = \int_0^\infty n(\varepsilon)d\varepsilon = \int_0^\infty \frac{D(\varepsilon)d\varepsilon}{\exp\left[\frac{\varepsilon-\mu}{kT}\right] + 1} \tag{16.9}$$

From eq. (16.7), noting that $\varepsilon < \varepsilon_F$, at absolute zero we have

$$\begin{aligned}
N &= 4\pi \int_0^{\varepsilon_F} \left[\frac{2m_e}{h^2}\right]^{3/2} V\varepsilon^{1/2}d\varepsilon \\
&= 4\pi \left[\frac{2m_e}{h^2}\right]^{3/2} V\frac{2}{3}\varepsilon_F^{3/2}
\end{aligned} \tag{16.10}$$

This then gives

$$\varepsilon_F = \mu_0 = \frac{h^2}{8m_e}\left[\frac{3N}{\pi V}\right]^{2/3} \tag{16.11}$$

The internal energy at absolute zero is found similarly as

$$U_0 = \int_0^{\varepsilon_F} N(\varepsilon)d\varepsilon = \frac{3}{5}N\varepsilon_F \tag{16.12}$$

The pressure of the electron gas at absolute zero is then found from $PV = \frac{2}{3}E_{tr}$ as

$$P_0 = \frac{2}{5}\frac{N\varepsilon_F}{V} \tag{16.13}$$

So fermions produce positive pressure, even at absolute zero, and have non-zero internal energy.

16.3   The Fermi Temperature

We can relate the Fermi energy to an equivalent temperature

$$\varepsilon_F = k\theta_F \tag{16.14}$$

Putting in typical densities of free electrons in eq. (16.11), we find that

$$\theta_F \approx 10^5 \text{ K} \tag{16.15}$$

Because most temperatures will be so much lower than this, the properties obtained at absolute zero will still apply to many higher temperatures. The electron energy and pressure are thus very large. The electrons also contribute to the specific heat, which is found to be

$$\frac{c_v}{R} = \frac{\pi^2}{2}\frac{T}{\theta_F} \tag{16.16}$$

which is correspondingly negligible at typical temperatures.

16.4   Reversible Work and Heat

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From statistical thermodynamics

$$dU = d\left(\sum_j N_j\varepsilon_j\right) = \sum_j \varepsilon_j dN_j + \sum_j N_j d\varepsilon_j \tag{16.17}$$

From the first law

$$dU = TdS - PdV \tag{16.18}$$

From statistical thermodynamics

$$P = -\sum_j N_j\left(\frac{d\varepsilon_j}{dV}\right) \tag{16.19}$$

Relating these to reversible work and reversible heating, we have

$$\delta W_{rev} = -\sum_j N_j d\varepsilon_j \tag{16.20}$$

and

$$\delta Q_{rev} = \sum_j \varepsilon_j N_j \tag{16.21}$$

Interpreting the first law from the perspective of statistical thermodynamics, reversible work requires a change in quantized energy, with no change in population, whereas reversible heating occurs by a change in population with no change in quantized energy. It doesn't matter whether the particles are distinguishable or indistinguishable for this.

16.5   Second Law

By considering the heating and work as separate processes microscopically, we can show that heat cannot be converted to work without any other change, because that would imply irreversible changes in the both the energies and populations of the different energy levels.

Lecture 17: Entropy and Information

17.1   The Boltzmann Definition of Entropy

In our usual notation, we found that

$$\frac{N_j}{N} = \frac{e^{-\frac{\varepsilon_j}{kT}}}{Z} \tag{17.1}$$

This can be interpreted as the probability of occurrence, P_j, of energy state ε_j.

The connection to entropy can then be written

$$dS = \frac{\delta Q_{rev}}{T} = \frac{\sum_j \varepsilon_j dN_j}{T} = -k \sum_j \ln\left(P_j Z\right) d\left(P_j N\right) \tag{17.2}$$

Which reduces to

$$dS = -Nkd\left(\sum_j P_j \ln P_j\right) \tag{17.3}$$

and

$$S = -Nk \sum_j P_j \ln P_j \tag{17.4}$$

This is the Boltzmann definition of entropy, which holds for both distinguishable and indistinguishable particles.

Entropy changes when the probabilities change due to a change in temperature.

17.2   Information Theory

Shannon defined uncertainty (in a message) $U(W) = \ln W$, where W is the number of possible ways of coding random information. For example, the number of ways of arranging N letters from an alphabet of M letters is given by

$$W = \frac{N!}{\prod_{i=1}^{M} N_i!} \tag{17.5}$$

where N_i is the expected number of each letter in typical prose, given

$$\sum_{i=1}^{M} N_i = N$$

Assuming N is large, we can apply Stirling's approximation to get

$$\begin{aligned} U(W) &= N \ln N - N - \sum_{1}^{M} \left(N_i \ln N_i - N_i \right) \\ &= N \ln N - \sum_{1}^{M} N_i \ln N_i \\ &= \sum_{1}^{M} \left(N_i \ln N - N_i \ln N_i \right) \\ &= -N \sum_{1}^{M} \frac{N_i}{N} \ln \frac{N_i}{N} \end{aligned} \tag{17.6}$$

Defining $P_i = \frac{N_i}{N}$ as the probability of getting letter N_i, we have

$$\begin{aligned} U(W) &= -N \sum P_i \ln P_i \\ &= -NI \end{aligned} \tag{17.7}$$

where Shannon defined information as

$$I = \sum_i P_i \ln P_i \tag{17.8}$$

Since

$$\sum dP_i = 0 \tag{17.9}$$

we can use a Lagrange multiplier as before to find the condition for minimum information as

$$dI = \sum \left[\ln P_i - \alpha \right] dP_i = 0 \tag{17.10}$$

Giving greatest uncertainty when

$$P_i = e^{\alpha} = \text{constant} \tag{17.11}$$

The least information, or greatest uncertainty, happens when all events are equally likely.

From the point of view of thermodynamics, maximizing the entropy of an isolated system identifies the system with the greatest uncertainty.

The probability of each state under conditions of thermodynamic equilibrium equals the inverse of the total number of states, which is total degeneracy summed over all levels. Eq. (17.4) then gives us

$$S = -Nk \sum_i P_i \ln \left(g^{-1} \right) = Nk \ln g \tag{17.12}$$

That is,

$$S = k \ln g^N = k \ln W \tag{17.13}$$

Our original Boltzmann statement of entropy also follows from considerations of equilibrium displaying the greatest degree of randomness, or the least amount of information.